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A STUDY OF THE REMOVAL OF SYNTHETIC ORGANICS FROM
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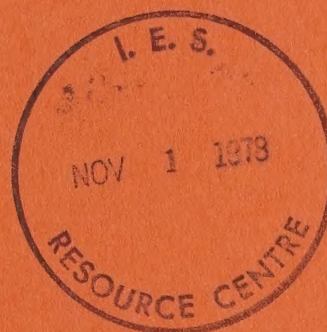
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a study of the removal of synthetic organics from drinking water by activated carbon



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A STUDY OF THE REMOVAL OF SYNTHETIC ORGANICS FROM
DRINKING WATER BY ACTIVATED CARBON

ENVIRONMENTAL HEALTH DIRECTORATE
HEALTH PROTECTION BRANCH

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ABSTRACT

The literature is reviewed with respect to the occurrence, health effects, and analysis of organic compounds present in potable water supplies. A wide array of potentially toxic or carcinogenic compounds are shown to exist in water. The properties of activated carbon are reviewed and carbon is shown to have the ability to adsorb the previously identified synthetic organics.

Activated carbon is widely used in the United States and Western Europe in potable water treatment. On the basis of field trips to three European water treatment plants and the literature of water treatment, the technology of activated carbon adsorption is reviewed. In general, in most plants, carbon is used for taste and odour removal, however, some European plants are now specifically operated for synthetic organic removal. Pretreatment by ozone is quite common in Europe and this is credited with improving organic removal by carbon by biological means. In general, yearly cost for carbon treatment for a typical Canadian family would be between \$2 to \$17, depending on the desired level of organic removal.

Studies on three Canadian water supplies indicate that potentially toxic compounds, such as polycyclic aromatic hydrocarbons, and chlorinated organics, are detectable in these supplies at levels similar to European water supplies where carbon is employed. Total organic carbon and chlorinated organics are well removed by carbon, however, some uncertainty exists at the present time with respect to polycyclic aromatic hydrocarbons. A

computed program has been shown to be capable of predicting continuous adsorption column data on the basis of simple batch tests.

RÉSUMÉ

La documentation scientifique est examinée en fonction de la présence, des effets sur la santé et des analyses des composés organiques que l'on retrouve dans les approvisionnements en eau potable. Il est démontré qu'un grand nombre de composés potentiellement toxiques ou cancérigènes sont présents dans l'eau. On étudie les propriétés du charbon activé et il est démontré qu'il peut adsorber les composés organiques synthétiques identifiés auparavant.

L'usage du charbon activé pour le traitement de l'eau potable est largement répandu aux États-Unis et en Europe occidentale. On examine la technologie d'adsorption du charbon activé en se basant sur des études effectuées sur le terrain à trois usines d'épuration des eaux en Europe et sur la documentation relative à l'épuration des eaux. En général, dans la plupart des usines, le charbon est utilisé pour enlever le goût et l'odeur: cependant certaines usines européennes l'utilisent particulièrement pour l'élimination des composés organiques synthétiques. Le pré-traitement à l'ozone est très fréquent en Europe et on lui attribue une amélioration de l'élimination des composés organiques par le charbon, grâce à une action biologique. En général, le coût annuel de l'épuration par le charbon pour une famille canadienne typique varie de \$2 à \$17, selon le degré désiré d'élimination des composés organiques.

Des études effectuées sur trois sources d'approvisionnements en eau au Canada indiquent que les composés potentiellement toxiques, tels les hydrocarbures polycycliques aromatiques et les organo-chlorés, sont détectables dans ces approvisionnements à des concentrations similaires à

celles des approvisionnements en eaux européens où l'on utilise le charbon pour le traitement des eaux. Si le charbon enlève effectivement le carbone organique et les organo-chlorés totaux de l'eau potable, il existe cependant présentement un certain doute relativement aux hydrocarbures polycycliques aromatiques. On a montré qu'un programme sur ordinateur est capable de prédire les données d'adsorption continu sur colonne en se basant sur de simples analyses de lots.

RECOMMENDATIONS

On the basis of this experimental study and review of the literature, the following recommendations can be made:

- (i) Studies should be undertaken to establish the health effects of organics in potable water.
- (ii) The use of granular activated carbon adsorption in potable water treatment should be promoted in Canada to insure safe and healthy potable water.
- (iii) The promotion of biological activity in activated carbon adsorbers should be examined further as such activity may offer substantial reduction in the cost to the consumer for activated carbon adsorption.
- (iv) The prediction of activated carbon treatment results and costs should be developed further on a wider range of Canadian water supplies to insure rational application of activated carbon adsorption.

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INTRODUCTION

During the late 19th century, slow sand (river bank) filtration was practiced in many European cities. Disinfection first by ozonation then chlorination was introduced in the first two decades of the twentieth century. Coagulation and rapid sand filtration was also developed by the third decade of this century. Technology has changed relatively little since then. The primary requirements for water treatment in Canada are still turbidity removal by coagulation and filtration and disinfection by chlorination.

The chemical process industry has also begun to develop during the early part of this century. This industry has enjoyed continued growth and, today, many new organic chemicals hitherto unknown to man and, therefore, potentially toxic are manufactured by this industry. Some of these materials are released to the environment and as shown below, with recent advances in analytical techniques, many such products have been detected in trace concentrations in the drinking waters of the world. The presence of these trace organics may pose long term potential health problems to man.

Activated carbon adsorption appears to be the most promising technology for effecting removal of such organics at acceptable cost. There are now thousands of water treatment plants in the world using powdered carbon and several using granular carbon adsorption. In Canada, there are relatively few plants using carbon for organic removal.

For example, there is only one, recently commissioned, plant in all of Canada using granular carbon adsorption in a permanent installation whereas more than forty United States plants use granular carbon.

The reasons for this relative lack of carbon plants in Canada may be:

- (i) the abundance of high quality water supplies,
- (ii) the relative lack of organoleptically oriented consumer demands, and
- (iii) some lack of technological expertise among plant designers and operators.

Government legislation, however, may eventually require organic removal as a precautionary health measure. In such case, background information will be required by government and industry alike.

Thus the purpose of this report is to:

- (i) assess the worldwide experience on organic removal by activated carbon,
- (ii) assess the potential use of carbon on some Canadian water supplies, and
- (iii) develop methods of interpreting non-Canadian data to Canadian water supplies.

The report is subdivided into three parts. The first part is a compilation of background data on water organics and activated carbon. This part is background to parts two and three. Part II is a survey of non-Canadian plant data along the lines of objectives 1 and 3. The third part summarizes studies done at McMaster University along the lines of objectives 2 and 3.

I-1 Organics in potable water supplies

I-1.1 Occurrence

I-1.1.1 Natural Organics

Humic substances constitute the largest fraction of organics in surface water. Visser (1972) indicated that the concentration of humic compounds found in lakes and rivers can be as high as 13 mg/l. Swampy lakes may contain as much as 30 mg/l of humic substances. Humic substances are stable compounds with molecular weights between 200 to 100,000 containing aromatic aldehyde, pentose, hexose and hydroxy groups as well as proteinaceous substances (Conn, 1963). The humic substances are responsible for the brownish-yellowish colour of some water. Decayed plant material is the source of humic substances.

Colour of the water is one problem facing water treatment plants, odour is another. The musty earthy odour has been traced to natural causes particularly to a product of actinomycetes by Bedeker et al. (1969), Hansen (1964) and Wood and Snoeyink (1970). Two objectionable products of actinomycetes are 2-exo-hydroxy-2-methylborneol and geosmin, both compounds are similar to camphor. The odour threshold concentration in water for these compounds is very low (0.1 µg/l probably due to their extremely high volatility. Hansen (1964) also related these compounds to taste along with odour problems.

Polynuclear aromatic hydrocarbons (PAH) are also present in surface waters. This is a heterogeneous group of chemicals, some of which are proven and most of the others are suspected carcinogens. Until recently, evidence has indicated that these compounds form at high temperatures, about 700°C, in an atmosphere that does not allow complete oxidation. Such conditions are often found in industrial furnaces and

internal combustion engines. Nonetheless PAH have been found in forest soils remote from human habitation. The concentration in soils is 100-1,000 $\mu\text{g}/\text{kg}$. Furthermore, the fresh water alga *Chlorella vulgaris* have been shown to synthesize several PAH. Many of the most important plants man uses as food synthesize and utilize PAH including the carcinogen, 3,4-benzpyrene and thus PAH is present in most water supplies, at levels between .025-.100 $\mu\text{g}/\text{l}$, depending on man's influence on the watershed. Andelman and Suess (1970) and Harrison, Perry and Wellings (1975) reviewed the extensive worldwide literature on these compounds.

The balance of the natural organics present in surface waters are waste products of biological activity. Visser (1972) presents an extensive list of amino acids, carbohydrates, peptides, proteins, phenolic compounds, lipids, fatty acids, hydrocarbons, sterols, estrogens, vitamins and lignins found in surface waters. Concentrations vary from detectable to the ppm range.

I-1.1.2 Presence of Organic Compounds in Surface Waters as Result of Human Activity

The list of investigators who identified and quantified organic compounds in potable water supplies is nearly endless and replication is common. A large number of papers are listed in the Bibliography. The scope of this report does not allow the review of any more than the directly relevant papers.

The US EPA's (1975) report to Congress lists 253 organic compounds found in U.S. drinking waters, and this list has since expanded greatly. Some of the compounds included, in general, are solvents, plasticizers, pesticides, herbicides, surfactants, halogenated organics, PAH, oils as

well as naturally produced compounds at concentrations in the $\mu\text{g/l}$ range. A list of selected contaminants and their range of concentrations is shown in Table I-1.1. The presence of synthetic organics in waters is not limited to North America. Meijers (1974) found the identical compounds in the same concentrations in the rivers Rhine and Maas. Grob and Grob (1974) working with water from Lake Zurich list 136 organic compounds with the unidentified compounds attributed to natural odour compounds, and humic substances. Of the identified organics, automobile fuel was the most widespread material found in water. They postulated that the transport mechanism of gasolines into water is by way of evaporation and direct transfer into water. Of solvents, the chlorinated solvents are more prevalent in waters due to their slow breakdown, especially tetrachloroethylene. Various industrial chemicals, found but not completely resolved on the GC column, were plasticizers. Grob and Grob also found some substances of natural origin such as C_{15} and C_{17} alkanes and alkenes, terpenes and organic sulphur. The concentrations encountered were in the ng/l to $\mu\text{g/l}$ range.

The source of brominated organics is stated by Rook (1976) to be the combustion of antiknock compounds in automobile fuels.

Increase in organic content of surface water was correlated with agricultural runoff by Morris and Johnson (1976) by measuring the chloroform concentration in finished tap water. In the spring and the fall, during snow melt and rainy seasons, the chloroform concentration rose to $230 \mu\text{g/l}$ while in the dry seasons, the concentration was $50 \mu\text{g/l}$. The higher chloroform concentration in the finished water were postulated to be caused by the higher concentration of organic precursors in the raw water from agricultural run-off.

TABLE I-1.1 (from EPA, 1975)

SELECTED CONTAMINANTS IN U.S. DRINKING WATER SUPPLIES

<u>Contaminant(s)</u>	<u>Concentrations in $\mu\text{g}/\ell$</u>	<u>Estimated Distribution*</u>
Carbon Tetrachloride	<2 - 3	10%
Chloroform	<0.1 - 311**	100%
Other Halogenated C ₁ and C ₂	<0.3 - 229	100%
Bis(2-chloroethyl)ether	0.02 - 0.12	low
β -chloroethylmethylether	unknown	low
Acetylenedichloride	<1	low
Hexachlorobutadiene	$\sim$ 0.2	low
Benzene (inc. Alkylated Benzenes to C ₆)	<10	high
Octadecane	$\sim$ 0.1	high
C ₈ -C ₃₀ Hydrocarbons	<1	high
Phthalate Esters	$\sim$ 1	50%
Phthalic Anhydride	<0.1	low
Polynuclear Aromatics	0.001 - 1	high

*These distributions for drinking water contaminants represent very rough estimates made by the Ad Hoc Study Group of the Science Advisory Board.

**The maximum chloroform concentration of 366 $\mu\text{g}/\ell$ found in Region V survey was not known at the time of the Board's review.

In the same manner, pesticides enter surface waters and eventually drinking water supplies. McNeil et al. (1977) found fourteen chlorinated pesticides in Ottawa tap water in concentration on the order of ng/l.

Wastewater effluents are a rich source of varied organics to contaminate surface waters (Chudoba, 1975). The organics found were bio-refractory as BOD/COD (i.e., Biochemical versus Chemical Oxygen Demand) ratio was less than 0.1. However fatty acids, proteins, polysaccharides were present. The same 60-70% of the organics were shown by DeWalle and Chian (1974) to be humic substances. Bertrand's (1974) review of organics in secondary effluent is shown in Table I-1.2.

The practice of chlorinating wastewater treatment plant effluents was shown by Jolley (1975) to produce a wide range of chlorinated organic compounds. He found about 50 (17 identified) compounds of total concentration of 20-100 $\mu\text{g/l}$ depending on the nature of the wastewater and chlorine or hypochlorite use. Concentrations with hypochlorite were near the lower end of the concentration range. The most prominent compound found was 5-chlorouracil or 4-chlororesorcinol known to be toxic to fish (see Tsai, 1968).

I-1.1.3 Interaction of Natural and Synthetic Organics

A review by Khan (1972) points out that pesticides, fatty acids, alkanes and dialkyl phthalates have been isolated from humic substances. Mechanisms to incorporate such substances into the humic matrix can be physical adsorption, ion exchange, hydrogen bonding, charge transfer, ligand exchange and chemisorption or the combination of all of the above. It is also possible that a peripheral or functional group of the humic substances interact with hydrophobic organics. Sodium humate has been

TABLE I-1.2 (from Bertrand, 1974)

Soluble Organic constituents
in Secondary Effluents.

CONSTITUENTS	PAINTER ET AL % OF CARBON	BUNCH ET AL % WEIGHT OF CONST.	REBHUN & MANKA % OF COD
CARBOHYDRATES ¹	1.5	5.0	13.7
PROTEINS ²	2.0	10.0	28.4
SOLUBLE ACIDS ³	12.0	-	-
ANIONIC SURFACTANTS ⁴	10.0	10.0	11.3
TANINS AND LIGNINS ⁵	-	5.0	1.5
HUMIC SUBSTANCES	-	-	36.6
ETHER EXTRACTABLES	-	10.0	8.5
UNIDENTIFIED	74.0	65.0	0.0

1 As glucose

2 As bovin serum albumine

3 As acetic acid-propionic acid in proportion 3:1

4 As A.B.S.

5 As tannic acid

shown to act as a surfactant thus solubilizing otherwise insoluble organics, such as DDT, and, therefore, it can be concluded that humic substances can act as pesticide carriers. As the result of the above revelations, it is conceivable that the quantities of pollutants in water are under estimated. On the other hand, pollutants adsorbed to humic substances may not be available to plant and animals. Interestingly, however, Malleval (1974) observed slight increases in pesticides in water after ozonation. Thus oxidation of the humic chain, by ozonation during water treatment, can release pollutants and, in the case of chlorination, further chlorinate them.

Many apparently toxic chemicals such as acrylonitrile, oxydipropionitrile and acrylamide monomer are broken down by biological action as shown by Cherry et al. (1956). Thom and Agg (1975) compiled a list of substances and their expected biodegradability. Many industrial chemicals, ordinarily considered non-degradable, can be degraded in biological systems with suitable acclimatization. Complete biodegradation however may not be possible due to everpresent variations in the operating conditions of the biological system (see Howe, 1976).

I-1.1.4 Organic Compounds in Finished Water

As the 253 organics listed in the EPA's (1975) report to Congress indicate many organic compounds can be found in tap water, most of these compounds were doubtless present prior to treatment. Some compounds, particularly chlorinated organics, on the other hand, can be created during treatment, namely, chlorination is believed to produce halomethanes (EPA, 1975: Stevens et al., (1976) and maximum chloroform concentrations of 366 $\mu\text{g/l}$ have been found (Table I-1.1). EPA and Stevens consider all organics in surface water as potential precursors

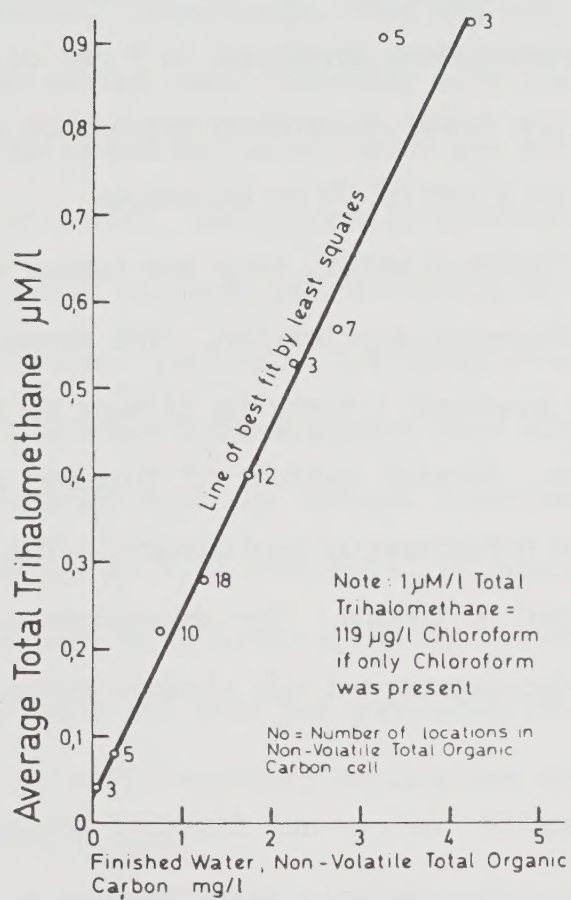
for the formation of halogenated organics.

Rook (1974, 1976) has extensively studied the formation of haloforms. He found that there is a seasonal variation in the production of haloforms. In the summer when the water is most coloured, the chloroform content of the finished water was 40-50 $\mu\text{g/l}$ while in winter chloroform concentrations were only 6-10 $\mu\text{g/l}$ at the Berenplaat treatment plant using water from both the rivers Rhine and Meuse. The colour of the water was caused by the presence of humic substances, thus humic substances appear to be probable precursors for haloforms. This was further confirmed when the chlorination of non-polluted natural water taken from a lake in a peatty region produced peak chloroform concentration of 200 $\mu\text{g/l}$ level. The colour of the peat bog water was two and a half times that of stored river water. Rook considers this as definite proof that the chlorination of natural coloured waters, containing humic substances lead to the formation of chloroform and other halo methanes. As most organics in water are believed to be humic in nature, production can be directly related to non-volatile organic carbon level as shown in Figure I-1.1.

I.1.2 Health Effects

In their report to Congress, EPA (1975) included the analysis of 80 drinking waters for six organics: chloroform, carbon tetrachloride, bromodichloro methane and dibromochloro methane, 1,2-dichloroethane and bromoform. All waters contained all six chemicals, in the majority of the waters the finished water contained all six chemicals, in the majority of the waters the finished water contained greater quantities than the raw water. Three of the six trihalomethanes, chloroform, carbon tetrachloride and dichloroethane have carcinogenic activity (Kraybill, 1975).

FIGURE I-1.1. DEPENDENCE OF THE AVERAGE CONCENTRATION OF TRIHALOMETHANE COMPOUNDS ON THE CONCENTRATION OF DISSOLVED ORGANIC CARBON (FROM SONTHEIMER, 1976)



Chloroform is the most prominent organic in drinking waters involved with hepatoma production. Of the 253 chemicals listed by EPA, 21 have animal carcinogenic activity, 4 are known carcinogens and many of the others are suspected carcinogens.

Chloroform and alcohol extracts of raw and finished waters were tested for their carcinogenic activity by Hueper and Payne (1963) and Hueper and Ruchoft (1954). Tumors were developed in 5 out of 72 mice by subcutaneous applications of the dried chloroform extract of raw waters dissolved in tricaprylin and in 2 out of 72 by cutaneous application. In the case of finished water, only two tumors were developed by subcutaneous and none by cutaneous application. The application of alcohol extracts of raw water produced 1 tumor in 72 mice by subcutaneous and 1 in 72 by cutaneous means. Alcohol extract of finished water only produced 1 tumor in 72 mice by subcutaneous application. The control and chloroform applications produced no tumors. The chloroform extracts contained chiefly aromatic hydrocarbons and the alcohol extract phenolics and detergents.

The chloroform extracts of the raw and finished waters caused upon repeated subcutaneous injection, spindle cell sarcomas at the site of administration in several mice. One of the mice in the raw water series developed papilloma of the bladder mucosa. Several mice in the series had neoplastic reactions of the lymphoid and reticulo endothelial system. The authors consider these reactions the actions of weak carcinogens. Nevertheless, they incriminate the water treatment process for allowing the carcinogenic chemicals through.

Eventhough the presence of PAH has been noted by several authors, their carcinogenic activity is widely debated. Pullman (1974) summarizes the diverse opinions of mechanism of carcinogenesis while Malling and Chu (1974) developed a mutational model to study carcinogenesis. These two papers present serious implication to potable water supplies with an abundant variety of organics. Eventhough, some PAH are known to be carcinogenic, many carcinogens cannot react directly with the biological target molecules DNA and RNA. The potential carcinogens are activated chemically by some yet unidentified system, catalytically by biochemical compounds, enzymatically by microbial enzymes, metabolically by liver microsomes and in host-mediated assays. In tests, 3,4 benzpyrene has shown negative results while 3-hydroxy-3,4-benzpyrene gave slight but significant increase in mutation frequency over the control experiments. The highest mutation frequency was shown by 9,10-dimethyl-1,2-benzanthracene. A defensive reaction of the body will convert the PAH to something that is easier to expell from the body and this new substance could be a stronger carcinogen than the original PAH. Further, Malling and Chu conclude that most carcinogens are mutagens.

Another paper by Shimkin (1968) indicated that the high frequency of both bladder and lung cancer is not entirely accountable to smoking or to air pollution. Mes et al. (1977) found eleven chlorinated pesticides and PCB in the human adipose tissue at concentrations of .4 $\mu\text{g/gm}$ wet tissue on the average. Interestingly, while the 26-50 age group had higher concentration than the 0-25 year age group, the 51+ years age group had slightly lower concentration than the 26-50 age groups, quite possibly due to the relatively recent introduction of these

chemicals. Four out of the 13 pesticides listed have been found in drinking water (see EPA, 1975).

Akiyama et al. (1975) found PCB at 2.8 ppb in maternal and 1.1 ppb in cord blood on wet basis and .36 and .22 respectively on fat basis.

The EPA (1977) considers PCB a suspected carcinogen and the chlorinated pesticides found in human adipose tissue by Mes (1977) either suspected carcinogenic or toxic compounds.

I-1.3 Organics Classification Methods

I-1.3.1 Total Organic Carbon (TOC)

The total organic carbon content of a sample of water can be measured as a quantitative rather than a qualitative indication of potential organic contamination.

Total Organic Carbon (TOC) is normally evaluated by direct combustion of a small water sample and the subsequent measurement of the CO_2 produced in the combustion. Previously, the commercial TOC apparatus were unable to measure accurately in the few mg/l range. Recently, however, advances in technology led to the development of several instruments (from Phase Separation Ltd., United Kingdom and Dohrman's Instruments, Santa Clara, Ca) apparently capable of such measurement. In addition, Addie (1973), Goulden (1976), as well as Brooksbank (1975) working in Canada, developed such systems from Technicon subunits (Technicon Corp.).

In addition, ultraviolet absorbance at 253.7nm the sharp spectral line of a low pressure Hg Lamp has also been shown correlatable to total organic carbon. Dobbs et al. (1972) correlated absorbance in a 1 cm cell ($A_{254 \text{ nm}}^{1 \text{ cm}}$) in waste water and $A_{254 \text{ nm}}^{5 \text{ cm}}$ in potable water application.

This system is not reliable in wastewater quantitative applications due to the high concentrations of inorganic UV absorbers and the quantitative presence of organics which do not absorb UV light. In raw and treated surface waters such interferences were not observed, thus reliability and correlations are excellent. Turbidity in the waters however does interfere as particles scatter light.

The level of TOC encountered in water supplies is generally between 0.05-12 mg/l (EPA, 1975).

I-1.3.2 Total Organic Chlorine

Chlorinated organics, as a class is perhaps the most significant subset, from a health point of view of the organics found in water. Thus a measurement of all of organic chlorine (TOCl) in drinking water would offer a qualitative as well as quantitative acceptability.

A system developed by Kuhn and Sontheimer (1973) utilizes carbon adsorption to collect and concentrate the organics from water. The loaded carbon is pyrohydrolyzed at 900°C and the resulting HCl collected (in HNO_3 solution and H_2O_2) and analyzed for Cl^- . The suggested carbon preparation is to desorb the inorganic Cl^- with NaNO_3 solution and subtract the inorganic Cl^- value from the Cl^- value obtained by pyrohydrolysis, thus obtaining the organic Cl^- . Typical values obtained are 0.1-0.2 mg Cl^-/gm activated carbon.

I-1.3.3 PAH

Borneff and Kunte (1969) determined PAH in water utilizing thin layer chromatography. The procedure involves extraction from a large water sample by cyclohexane or benzene, concentration of the extract, and developing the extract spots with n-hexane-benzene in the first direction and methanol-ether-water in the second direction on TLC plates made of Al_2O_3 -silica gel-acetylated cellulose. The developed plates are viewed under 366 nm light and the location of the sample-spots are compared qualitatively with standards. This method as developed by Borneff is the standard method used in EEC countries.

The visual detection used by Borneff is not satisfactory as there may be many parameters affecting the location and the size of the spots on the plates. Bender (1968) dissolved the spots and analyzed the solution with a scanning spectrophoto-fluorometer. The sample spectra are compared with the spectra of pure PAH, and the UV absorbance or fluorescence may be calibrated according to concentrations. Tomingas et al. (1977) identified PAH's with a VIS-UV chromatogram analyzer directly on the plate at characteristic excitation and emission wavelengths. To measure the amount of PAH present, the sample spot area was compared to the corresponding standard. Hood and Winefordner (1968) dissolved the sample spots with ethanol, cooled the solution to 77 °K (liquid nitrogen) and obtained characteristic fluorescence and phosphorescence excitation and emission wavelengths. Identification was made by comparison to pure PAH. Quantitative measurements were obtained by calibrating the instrument with known amounts of pure PAH.

The use of spectral analysis is shown by Sawicki (1966) to be very useful when substituted PAH and heterocyclic aromatics are also present.

I-1.3.4 Specific Identifications - Gas Chromatography

Gas chromatography is a widely used method to identify and quantify individual organic compounds. Conditions such as column temperature, column medium, gas flow, detection and the extraction solvent to elute a group of organic chemicals are generally unique to each individual compound. Therefore, it is beyond the scope of this report to discuss the application of GC to various groups of organic chemicals. However, a partial list of authors and their application of gas chromatography is provided below:

Chlorinated organics in water:

Stevens and Symons (1974)
 Nicholson and Meresz (1975, 1976)
 Mieure (1977)

Organic substances in potable water:

Grob (1973)
 Bellar and Lichtenberg and Kram (1974)
 Kleopfer and Fairliss (1972)
 Cowen et al. (1975)

Bio-(2-Chloro) ethers and Dieldrin:

Dressman and McFarren (1976)

Vinyl chloride:

Dressman and McFarren (1976)

Benzo(a) Pyrene:

Davis (1968)

C₂-C₅ acids in water:

DiCarcia and Samperi (1974)

Dimethylformamide and dimethylamine:

Kubelka et al. (1976)

Di(2-ethylhexyl) Phthalate:

Weisenberg et al. (1975)
 Mayer et al. (1972).

I-1.3.5 Gas Chromatography/Mass Spectrometry

A powerful extension of gas chromatography is its coupling to a mass spectrometer equipped with computerized library of spectra and computer program of spectra interpretation, see McGuire et al. (1973), 1975), Suffet and Radzinul (1976) and Heller et al. (1975). The G.C. is used for separation and the M.S. for finger printing the GC eluant fractions. This system is absolutely necessary to characterize a complicated mixture of chemicals such as those found in a polluted river.

Bellar and Lichtenberg (1974) and Grob (1973) found it necessary to confirm their results from GC with MS. The water quality problems encountered in New Orleans were documented with GC/MS, see Dowty et al. (1975). Bonelli et al., (1975) applied mass fragmentography GC/MS to the identification of a wide range of water pollutants with improved sensitivity over the standard flame ionization detector.

The MS was interfaced through a dimethylsiloxane polymer membrane with a liquid chromatograph by Jones and Yang (1975). The membrane transmits non polar solutes and rejects polar solvents. With this system higher molecular weight low volatility compounds can be detected, such as PAH and metabolites.

I-1.3.6 Direct Spectrophotometric Methods

Schwarz and Wasik (1976) studied the excitation and fluorescence of several PAH in water at concentration levels encountered in raw and treated surface waters. Each PAH had unique spectra that was discernible even in a mixture. The fluorescence was concentration dependent thus

concentration calibration is possible. Oxygen quenching of the fluorescence in the water was no greater than 30%.

D'Silva et al. (1976) obtained optical luminescence of PAH with X-ray excitation. The PAH (from either the end result of extraction from water or from TLC plates) were dissolved in n-alkanes and frozen at 77 °K. The spectra are identical to the ones listed by authors using UV excitation. X-ray excitation has the advantage of eliminating the optical "cross-talk" between exciting and luminescence radiation encountered with UV excitation.

Van Geel and Winefordner (1976) used pulsed N₂ laser to excite PAH and aromatic compounds. Fluorescence and Raman spectra were recorded. Eventhough the laser excited at 337 nm, and not at the characteristics exitation wavelength of PAH, the emission characteristic wavelengths were not substantially different from previous data where the characteristic excitation wavelengths were used.

I-1.3.7 Other Methods

Whitrack (1975) used single-sweep polarography to determine water contamination. Besides inorganics, the water was spiked with explosives, plasticizers and solvents. Apparently, the contaminants form a characteristic trace on the current versus voltage plot. Concentrations shift the traces. Small samples are required and sensitivity is on the order of µg/l.

With plasma chromatography, Karasek (1971) analyzed PCB utilizing ⁶³Ni beta source to produce ions which, in turn were injected into a MS. The mass-plasmograms thus produced are characteristic of individual PCB.

I-1.3.8 Extraction and Concentration

Work by EPA (see Buelow et al., 1973) developed the use of activated carbon to collect and concentrate organics from water. The organic recovery was achieved by chloroform extraction. The method is known as the mini-CAM-CCE method. This method has fallen into dis-favour as the chloroform extraction was shown to have low efficiency by Capelli et al. (1976) while carbon adsorption efficiency was excellent. Activated carbon is used in the TOCl method, also.

Several authors, Harvey (1973), Burnham et al. (1972), Svec et al. (1974), Leenher and Hoffman (1976), Junk et al. (1974) and Ahnoff and Josefsson (1974), have used macroreticular resins to collect and concentrate the organics. After extraction from the resin, various modes of analyses were followed such as : GC, GC/MS, spectrophotometry and gross organic weight determination. Junk et al. (1974) achieved excellent recoveries for a wide range of organic compounds.

Both Klein et al. (1975) and Deinzer et al. (1975) attempted to concentrate the organics in water using reverse osmosis and semipermeable membranes. Results are inconclusive as membrane properties affect the type of organics rejected and concentrated. Furthermore, chemical reactions are possible between membrane and solute.

I-1.3.9 Methods of Analysis for Pesticides

All the analytical techniques described above have been utilized in the identification and quantification of pesticides. See: Pitt et al. (1974); Alford (1973); Breidenbach et al. (1966); Chau (1972); and Croll (1972).

I-1.4 SUMMARY

A review of the literature indicates that a wide variety of natural and synthetic organics can be present in potable water supplies. These include humic substances, taste and odour causing compounds polycyclic aromatic hydrocarbons (PAH), biological metabolites, industrial solvents, plasticizers, pesticides and herbicides.

Raw water organics appear to be somewhat reduced but not eliminated during treatment and, in the case of chlorinated organics substantial increases have been observed. The increase in chlorinated organics appears to be directly linked to the chlorination, during disinfection, of the water organics.

There has been substantial progress in recent years in the analysis of trace organics. There are several new commercial apparatus capable of measuring total organic carbon. A method has been suggested in the literature for measuring total organic chlorine and there are several reported methods for measuring PAH.

The combination of gas chromatography and mass spectrometry now allows direct identification of a wide array of volatile and moderately volatile organics and, through the use of liquid chromatography as pretreatment to mass spectrometry, the specific identification of non-volatile substances is now possible.

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I-2 ACTIVATED CARBON AS AN ADSORBENT

Potable water treatment with crude activated chars or charcoals began with the ancient Egyptians and continued through the ages. One of the first industrial records of a carbon filter applied to water is described by the London News of June 6, 1874, as "the self-cleaning charcoal filter, patented by the celebrated Lipscombe ... the only one that removed the disgusting sewage found in cistern water".

These early chars were mainly made by the oxygen limited burning of wood. Toward the late 19th century, the need for sugar decolourizing led to large scale adsorption installations and this in turn led to the significant enhancement of adsorptive power through activation (see Section I-2.1).

Thanks to activation, carbons have become a versatile and economic adsorbent of great significance to modern water treatment, as shown in Part 2. This chapter, prepares the way for the discussions of Part 3 by presenting the relevant properties of activated carbons. Much of the discussion in this chapter is based on an unpublished paper (Benedek, 1974).

I-2.1 Physical Characteristics

Activated carbon can be made from almost any carbonaceous material (e.g., wood, lignite, coal, coconut shell) by first using heat or heat plus dehydrating chemicals to liberate carbon from its associated atoms. This first step is known as carbonization. Subsequently, mildly oxidative hot gases (e.g., carbon dioxide or steam) at temperatures ranging from 600-1,700°F are used to activate the carbon. The process of activation refers to the removal through combustion of additional non-carbonaceous matter and the creation of tiny fissures or pores.

In the end, we obtain a material largely consisting of packets of microcrystallite of carbon. These microcrystallites are in turn composed of fused hexagonal carbon rings and average about $20\text{-}50\text{\AA}$ in maximum dimension (Wolf, 1959 and Scheffler, 1968). The fissures within and the space between microcrystallites constitute the pores.

The properties of activated carbons vary due to differences in starting material and activation procedure. Tables I-2.1 and I-2.2 summarize the properties of some of the activated carbons sold in Canada.

The first distinction among activated carbons is based on particle size. Thus activated carbons greater than 40 mesh are classified as granular (Table I-2.1) while those with average size below 325 mesh are known as powdered carbons (Table I-2.2). Contacting equipment and design procedures differ between powdered and granular carbons and they will be discussed separately in section 3 and 4.

An extensive explanation of the terms in Table I-2.1 and I-2.2, along with their detailed measurement procedures is presented in the appendix of the United States EPA (1973) Process Design Manual. The first seven properties in these tables are connected to adsorptive behaviour as shown below. The other properties influence design and cost considerations and their discussion will be included in a more appropriate chapter.

The major influence of starting material among the adsorptive properties is on ash content. The ash in carbon results from the inorganic constituents of the starting material and, therefore, naturally, a carbon made from lignite is going to have a much higher ash content than one made from petroleum residue. The ash content of the carbon can influence the adsorption of inorganic and polar organic compounds through ion exchange (Kipling, 1957).

TABLE I.2.1

A COMPARISON OF 8 x 30 COMMERCIAL GRANULAR CARBON PROPERTIES

PROPERTY	UNITS	CALCON FILTRASORB 300	ICI AMERICA HYDRODARCO 3000	AMOCO GX-31	WITCO 517
Raw Material		Bituminous Coal	Lignite	Petroleum	Petroleum
Surface Area, BET	m ² /g	950-1050	600-700	2200-2600	1050-1250
Average Pore Size	Å		28-33		
Iodine No., max.		950	600		1000-1200
Molasses No.			400-450		
Moisture, min.	%	2.0	9		1
Water Extractable	%		0.5-1.1		0.2
Ash Content	%		12-18	2.0 max.	<1
Apparent Density	g/cc		.39-.48		0.45-.54
Backwashed and Drained Density	lb/ft ³	26	22		27-28
Particle Density, Wetted in Water	g/cc	1.3-1.4	1.3-1.4		
Skeletal Density	g/cc		2.0-2.3	3	
Ave. Particle Size	mm	0.8-0.9	1.5		1.34
Uniformity Coefficient		1.9	1.9		1.55
Oversize, max. +8 mesh	%	15	4		5
Undersize, max. -30 mesh	%	5	1		5
Hardness					
Ro-Tap Abrasion	%	70	50-70		85
NBS Abrasion	%		<25		5
Cost FOB Toronto at July 1, 1974	Can. \$ lb.				
< 2,000 lb.	"	.51	.51		.48
<10,000 lb.	"	.49	.48		.44
<30,000 lb.	"	.47	.46		
>30,000 lb.	"	.46	.44		.40

TABLE I-2.2

A COMPARISON OF COMMERCIAL POWDERED CARBON PROPERTIES

Raw material	UNITS	ICI AMERICA HYDRODARCO C	AMOCO PX-21	WESTVACO* AQUA NUCHAR
Surface Area, BET	m ² /g	Lignite 550	Petroleum 2800-3500	Black/Liquor 600
Average Pore Size	Å	30	22.3	22.2
Iodine No.		585	2800-3600	700-800
Molasses No.		350(est)		
Moisture, max.	%	5		5
Water Extractables	%		1.0 max.	3-4
Ash Content	%	30	2.0 max	6.5
Particle Density, Wetted in Water	g/cc	1.35		
Apparent Density	g/cc	.34	.27-.32	.24-.27
Average Particle Size	μ	30		
-325 Fraction	%	70	86	90
Cost FOB Toronto at July 1, 1974	Can.\$ lb.			
< 2,000	"	.31		.24
<10,000	"	.28		.23
<30,000	"	.27		.22
>30,000	"	.24		.22

*Properties of July 1, 1974. A new Nuchar will be released late 1974.

The most important adsorptive property of an activated carbon is its extremely high surface area. As Table I-2.1 and I-2.2 indicate typical wastewater activated carbons possess surface areas between 600 and 1,100 m²/g, however, the recently developed Amoco carbons have surface areas previously imagined impossible. Their apparent surface area exceeds the maximum surface area formed by single atom walled pores. To visualize this phenomenal surface area, we can use the conventional analogy that 5g of a typical activated carbon has enough surface area for a football field. The importance of surface area to adsorption arises from the assumption that the number of adsorbable molecules per unit weight of adsorbent is linearly proportional to the surface area. Such linear relationship, however, is invalid if not all of the surface area is available to adsorbing molecules. The surface areas reported in Tables I-2.1 and I-2.2 are based on the adsorption of nitrogen. The nitrogen molecules, however, are only 4.3 Å in diameter (Scheffler, 1968) and adsorbing pollutants are often much larger. The iodine number and especially the molasses number are attempts to measure the surface area available to somewhat larger molecules. Thus the iodine number is believed to be proportional to the surface area in pores greater than 10 Å while the molasses number is proportional to pores beyond 28 Å (Juhola, 1951). The pores in activated carbon can be classified (Scheffler, 1968) as micropores (3-50 Å), transitional pores (50-1,000 Å) and macropores (>1,000 Å). The bulk of the surface area in activated carbons lie in the micropore range which tends to overlap the size range of most adsorbing pollutants. The surface area in the transitional range is relatively small, nonetheless, these pores become very important with large molecules such as lignins, proteins, etc. Finally,

the macropore range contribution to the surface area is negligible, however, their existence as diffusional passages is very important in granular carbons.

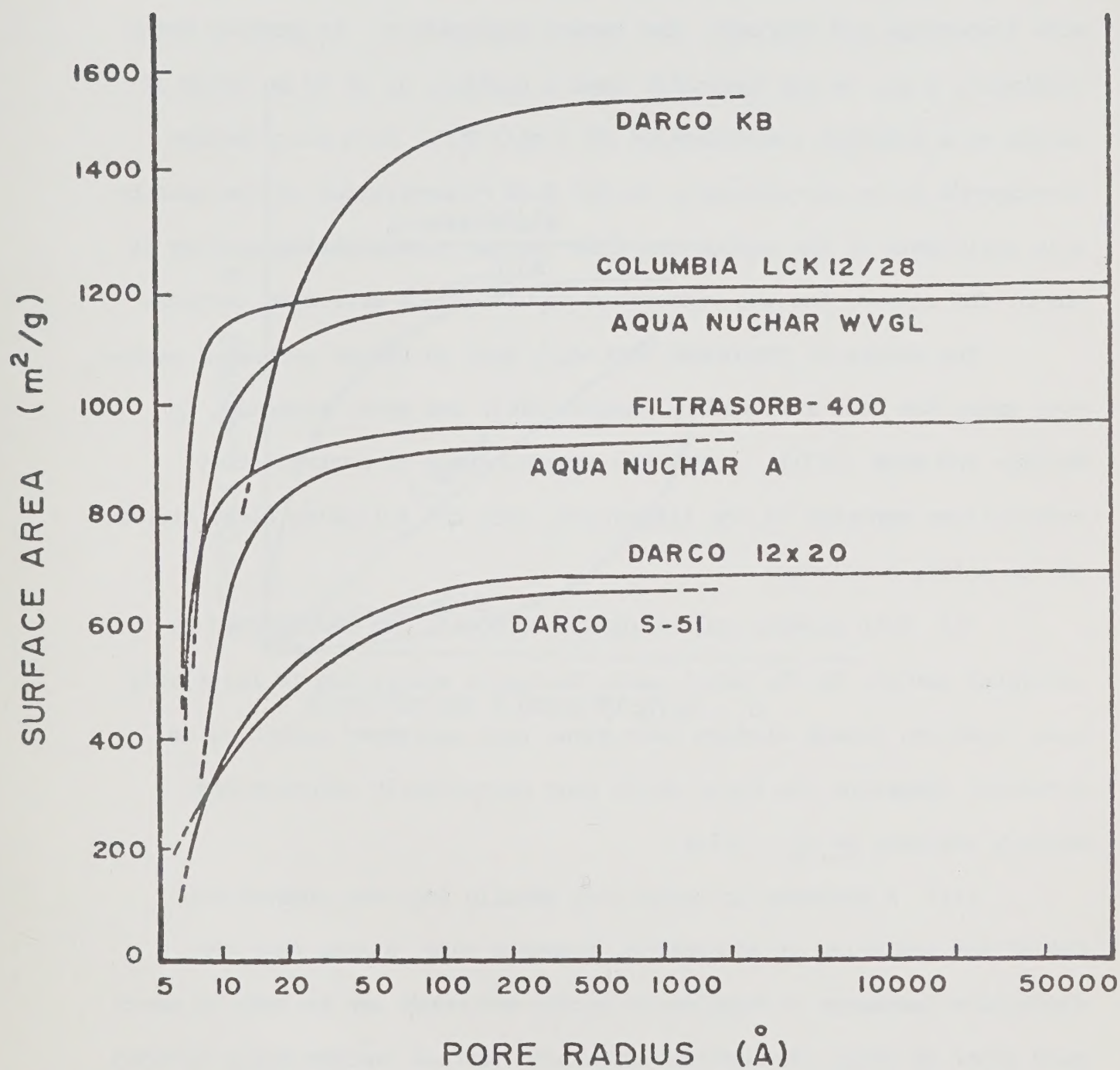
The distribution of surface area as a function of pore size has been measured by Rankin (1974) for many of the activated carbons in Tables I-2.1 and I-2.2. His results are shown in Figure I-2.1.

In adsorption, the nature of the adsorbing surface is also very important. During manufacturing, activated carbons tend to retain some of the hydrogen in the starting material. On cooling, oxygen from the surrounding air combines with carbon and hydrogen to form a mixture of polar surface groups such as carboxylic acids, lactones, chromones, phenols, etc. (Garten and Weiss, 1957). For example, for Nuchar C-190, Cookson and Ishizaki (1971) report that 0.3% of the total carbon surface area is occupied by carboxylic acid groups, 0.26 % by lactones, 1.06 % by quinones and 1.02 % by phenols. The presence of these surface groups results in a heterogeneous, part polar, part non-polar surface, thereby permitting a very wide array of substances to adsorb as discussed in the next section.

I-2.2 Adsorption Characteristics

Adsorption is attachment to a surface and it occurs because the adsorbate (the substance adsorbed) prefers the environment of the adsorbent (in our case, activated carbon) to the solvent (in our case, water). Typically, even if the carbon environment is strongly favoured, an adsorbate will not be completely adsorbed from solution. Instead, an equilibrium will develop such that the adsorbate will distribute itself between the carbon and liquid phases. A plot of such an equilibrium

FIGURE I-2.1. PORE SIZE DISTRIBUTIONS IN ACTIVATED CARBONS
(RANKIN, 1975)



distribution at constant temperature between the solid phase concentration or loading, q , and its equilibrium liquid phase concentration, c , is known as an adsorption isotherm.

Isotherms of pure compounds generally fit into one of the four types shown in Figure I-2.2-I-2.3. Isotherms on activated carbon are usually of the favourable type. The higher the value of q , at a given value of c , the more favourable and economic the carbon application. In potable water treatment, e.g., we may typically have a loading, q , of 40 mg TOC/g of carbon at a solution concentration of 3 mg/l TOC. Such distribution corresponds to an approximately 20,000 fold concentration of the adsorbable pollutants by the carbon and this immense concentrating ability is one of the reasons for the widespread popularity of activated carbons.

The nature of compounds that will tend to favour activated carbon over water has been reviewed by Hassler (1963) and more recently, by Mattson and Mark (1971). Among the many hundreds of contradictory observations reported in the literature, only the following clear trends can be safely concluded:

(i) Both organic and inorganic compounds can be adsorbed by activated carbon. In the usual case, inorganic adsorption is relatively poor, however, recent studies have shown that activated carbon is an excellent adsorbent for heavy metal ions particularly chromium and mercury (Behmann *et al.*, 1974).

(ii) A decrease in solubility usually improves adsorption. One of the few rules of adsorption, Traube's rule, states that the adsorption isotherms of homologous series compounds can be made to match each other by using reduced concentrations (actual concentration divided by solubility).

FIGURE I-2.2. ADSORPTION ISOTHERMS

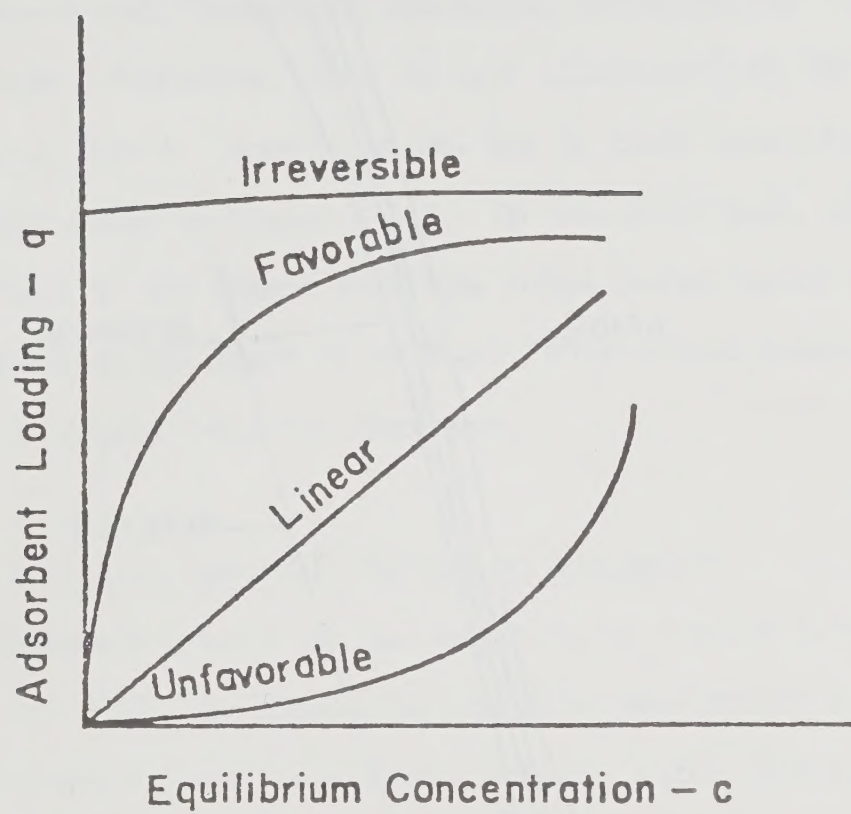
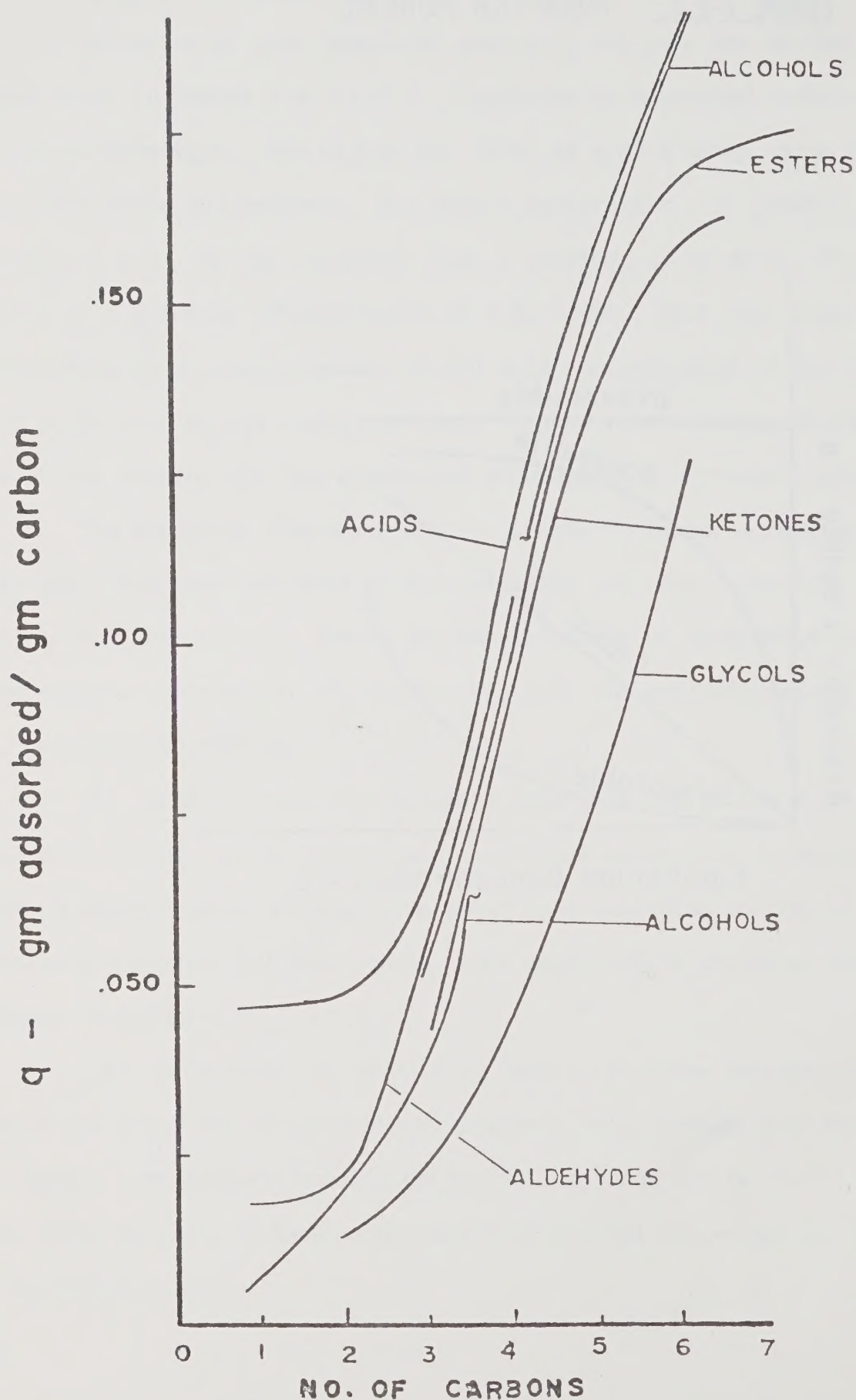


FIGURE I-2.3. THE EFFECT OF MOLECULAR WEIGHT ON THE ADSORPTION OF LOW CARBON NUMBER ORGANICS (GIUSTI ET AL., 1974)



(iii) Aromatic compounds generally adsorb better than aliphatic compounds with similar solubility.

(iv) Substituent groups such as hydroxyl, amino and sulfonic acid decrease adsorption while nitro tends to increase it.

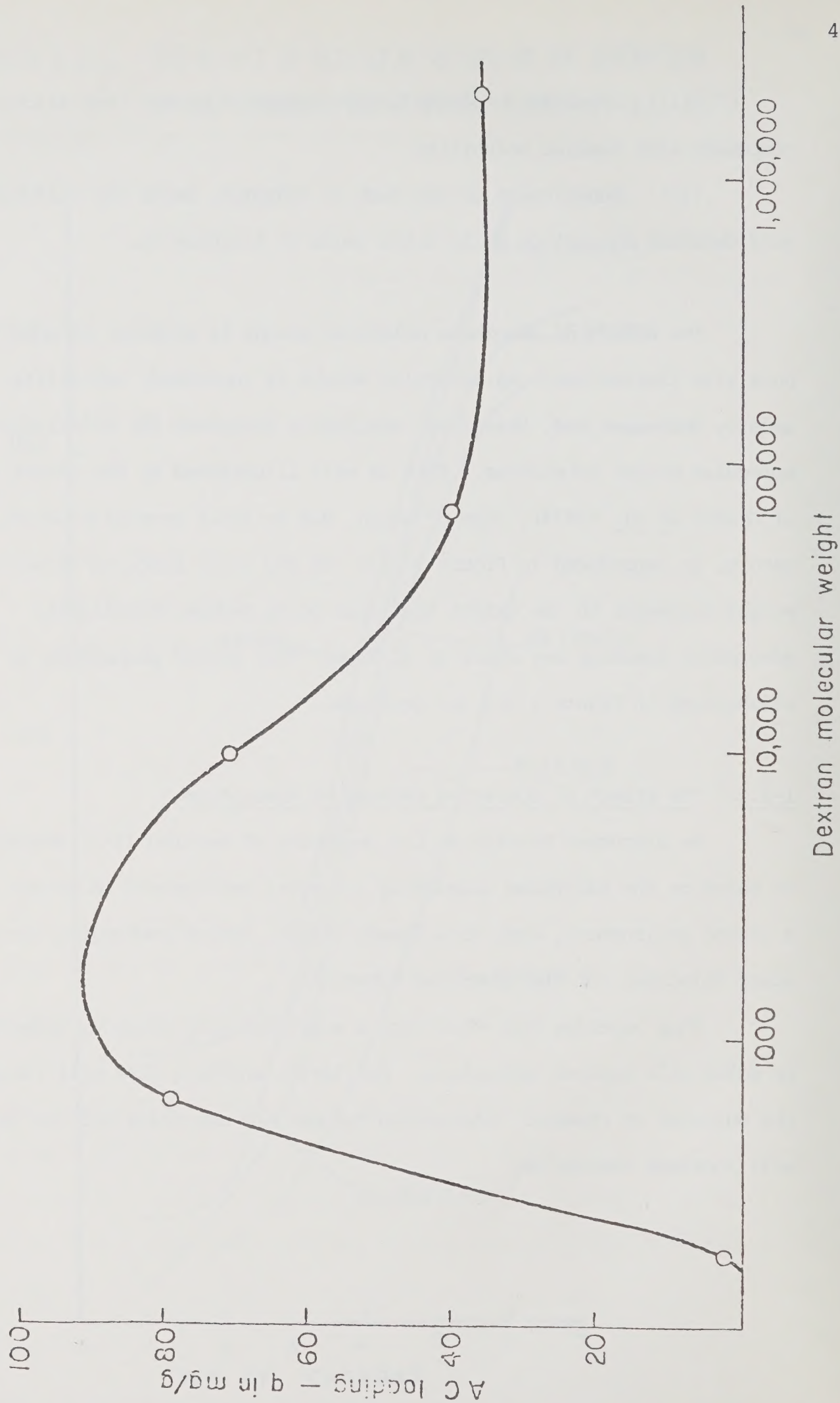
The effect of adsorbate molecular weight is somewhat clouded by pore size limitations. As molecular weight is increased, solubility usually decreases and, therefore, adsorption increases for relatively low molecular weight substances. This is well illustrated by the recent data of Giusti et al. (1974), some of which, due to their generally useful nature, is reproduced in Figure I-2.3. On the other hand, as molecular weight increases to the extent that some pores become unavailable, adsorption loadings may start to go down. This second phenomenon is illustrated in Figure I-2.4 for Dextran.

I-2.3 The Effect of Operating Factors on Adsorption

As discussed briefly at the beginning of section II-2, adsorption is based on the adsorbate abandoning its water environment in favour of a carbon environment, and, to a lesser extent, carbon exchanging surface water molecules for the adsorbing substance.

Thus anything that will make a substance less soluble, hydrated or polar will improve adsorption. Similarly, anything that will increase the physical or chemical interaction between the adsorbate and the carbon will increase adsorption.

FIGURE 1-2.4. THE ADSORPTION OF DEXTRANS ON AQUA NUCCHAR A
(ZGOLA, 1974)



Variation in pH

In water, the H_3O^+ ion concentration or pH determines the degree of ionization of weak acids and bases. Furthermore, pH is also the potential determining ion for colloids. Thus adsorbate polarity, and, often, solubility is strongly influenced by pH.

Most water organics and colloids contain acidic functional groups, and, therefore, reducing the pH will decrease ionization and improve adsorption. This has been shown for domestic wastewater by Morris and Weber (1966) and for weakly acidic wastes by Baker et al. (1972) among others.

Ward and Getzen (1970) studied pH effects during the adsorption on activated carbon of phenoxy acid herbicides. These weak acids ionize in the neutral pH range; in the case of phenolacetic acid, the reaction is as follows:



The capacity of the carbon for the neutral form of phenoxyacetic acid was observed by Ward and Getzen to be three times as high as for the ion. Interestingly, as the pH was lowered, improved adsorption started to be observed at pH below 6 where all of the acid should be still ionized as the reaction constant, pK_a , for the above reaction is only 3.3. This phenomenon was attributed by Ward and Getzen to hydronium ion adsorption forcing some adsorption of anionic species as electroneutrality always has to be maintained. Thus, it is quite likely that even a small drop below neutral pH will have significant benefits during the adsorption from water.

Surface Oxides

The chemical and physical interaction between adsorbates and the surface oxides of activated carbon is generally believed responsible for the adsorption of highly polar adsorbates. Thus Coughlin (1970) found that increasing the acidic oxides of activated carbon by chemical oxidation increases the adsorption of the highly polar urea molecule. The number and type of surface groups are influenced by activation temperature, with oxygen content increasing as the activation temperature is decreasing (Hassler, 1963). Mattson and Mark (1971) observed that a distinct optimum activation temperature exists for the adsorption of p-nitrophenol which is well below the activation temperature for maximum surface area.

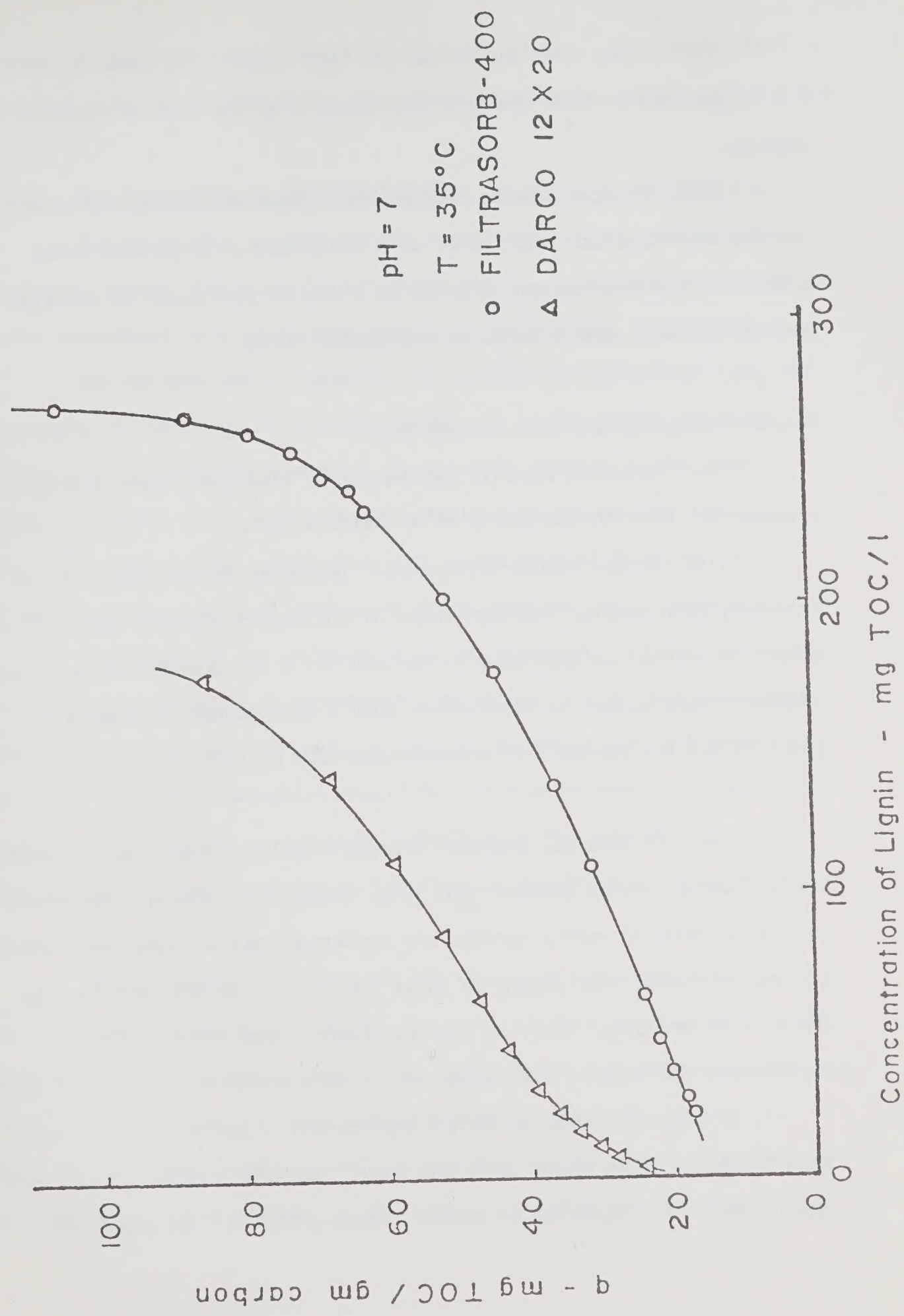
Carbon Pore Size Distribution

As discussed above, the fraction of pores available to an adsorbing molecule determines the effective surface area for adsorption. For larger molecules such as lignin much of the micropores where the bulk of the surface area tends to lie may be useless and a carbon with a low total surface area but high transitional pore area may prove superior (see Figure I-2.5). Furthermore, carbon pores tend to enlarge with prolonged activation or repeated regeneration and for very large molecules, we may want to deliberately effect this enlargement.

I-2.4 Powdered Versus Granular Carbons

Deciding whether powdered or granular carbon should be used in a prospective application is generally a difficult decision. The factors to be considered are:

FIGURE I-2.5. LIGNIN ADSORPTION ON DIFFERENT PORE SIZE ACTIVATED CARBONS
(RANKIN, 1975)



(i) Lower cost for carbon per unit weight. As shown in Section I-2.1, powdered carbons are generally about $\frac{1}{2}$ of the cost of granular carbons,

(ii) Lower equipment capital cost, powdered carbon contacting can proceed simultaneously with other unit operations. In potable water treatment, powdered carbon is added as a slurry just prior to settling whereas granular carbon requires a separate filter.

Factors favouring granular carbons are:

(i) Relative ease of regeneration. Powdered carbon regeneration systems are just now beginning to be commissioned.

(ii) Higher carbon efficiency. Depending on the shape of the isotherm, much greater loadings (mass of pollutants adsorbed per unit weight of carbon, defined as q in Section I-2.2 are possible with granular carbons. This effect is accentuated when a high degree of removal is required and the isotherm is unfavourable (see Section I-2.5).

Thus, in general, powdered systems require a lower capital cost while granular carbon systems tend to be cheaper to operate. Therefore, currently powdered carbon systems are preferred only in situations where the carbon dosage requirement is quite low and/or the effluent flow is small. On the other hand, as powdered carbon regeneration gains acceptance, the balance will swing toward more powdered carbon applications.

In general, powdered carbon application in water treatment are useful only in cases where taste and odour compounds removal is the only requirement. For organics in general, large prohibitively expensive

dosages of powdered carbon would be required. Hence, the subsequent chapters will be, on the whole, restricted to granular carbon applications.

I-2.5 The Evaluation of Activated Carbon for Specific Applications

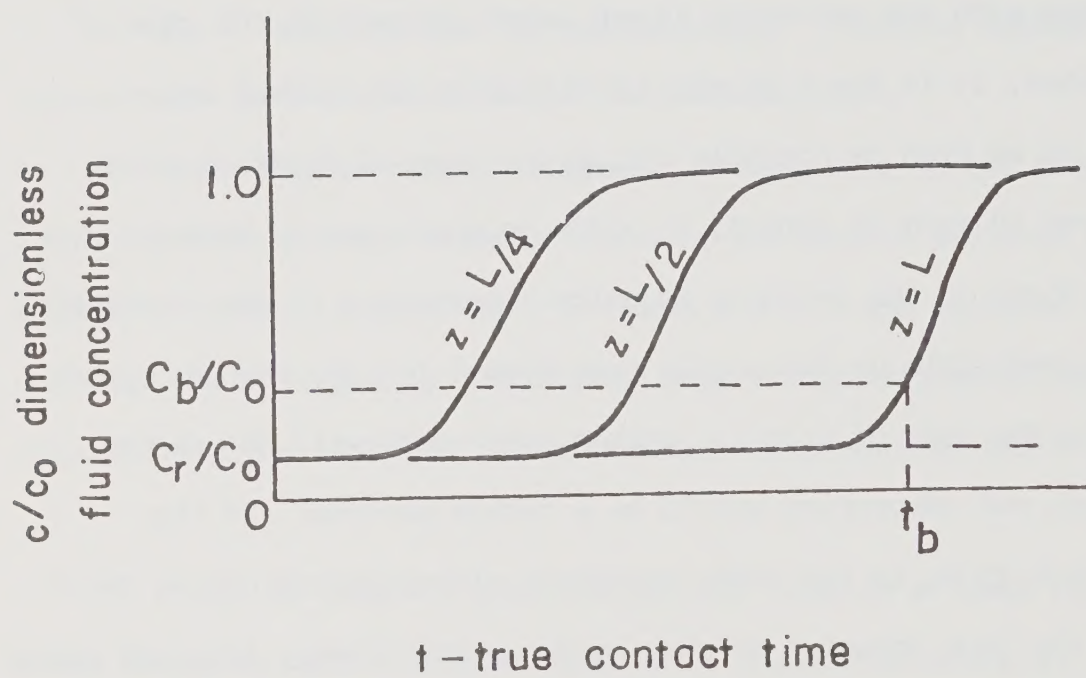
The first step in determining the potential applicability of activated carbon, for a particular water supply, is an isotherm run on water pretreated to a level anticipated in the eventual application.

The maximum carbon capacity can be directly determined from the isotherm. In the case of granular carbon, it is the carbon capacity, q , in equilibrium with the untreated (feed) water whereas in the case of powdered carbon, it is the q in equilibrium with the treated water. This should be as high as possible and in the case of drinking water, normally above 10 mg/g of carbon, to allow economic use of carbon.

The shape of the isotherm is quite important. If the isotherm is either irreversible or favourable (see Figure I-2.2), the adsorption wave front in the case of granular carbon contactors will not expand with bed depth and adsorption should be a viable process. If the adsorption wave front is too wide, adsorbers either adsorb only a small fraction of the feed organics or they become prohibitively long and expensive to operate.

The adsorption wavefront, is the region of declining concentration in a carbon bed (see Figure I-2.6). The width of this front is determined by the degree of favourability of the isotherm and the adsorption kinetics. Adsorption kinetics, in turn, are determined by the bulk liquid film mass transfer coefficient as well as the diffusivity of the adsorbate in the carbon particle itself. The bulk liquid film mass transfer

FIGURE I-2.6 ADSORPTION WAVES
(FROM PEEL AND BENEDEK, 1975)



coefficient is easily estimated from standard correlations (Geinkoples and Wilson, 1972). The intraparticle diffusion in turn must be measured by batch tests in which the declining of solution concentration after the addition of carbon is monitored as a function of time. The interpretation of such curves are explained in further detail in Section III-1.3.4, however, the faster the diffusion constant, the shorter the adsorption and the cheaper the application of carbon.

I-2.6 Adsorption Modelling

The most important use of kinetic data is adsorption modelling. Peel and Benedek (1976) generalized such a modelling to include biological activity around the carbon and proposed that there are three phases in a carbon column, namely, a bulk water phase, a biological film growing around each carbon granule (see Figure I-2.7) and the carbon phase itself. From a mass balance on a differential adsorber segment (Figure I-2.8), Peel and Benedek obtained

$$\begin{aligned}
 & -v_s \frac{\partial C}{\partial Z} - R_p \left(\frac{6 \cdot \delta}{p} (1 - \epsilon) \right) \\
 & = (\epsilon - (1 - \epsilon) \frac{6 \cdot \delta}{dp}) \frac{\partial C}{\partial t} + \rho_B \frac{\partial \bar{q}}{\partial t}
 \end{aligned}$$

where R_p = reaction rate per unit volume of film,

dp = carbon particle diameter,

$1 - \epsilon$ = volume fraction of carbon,

ρ_B = bulk carbon particle density,

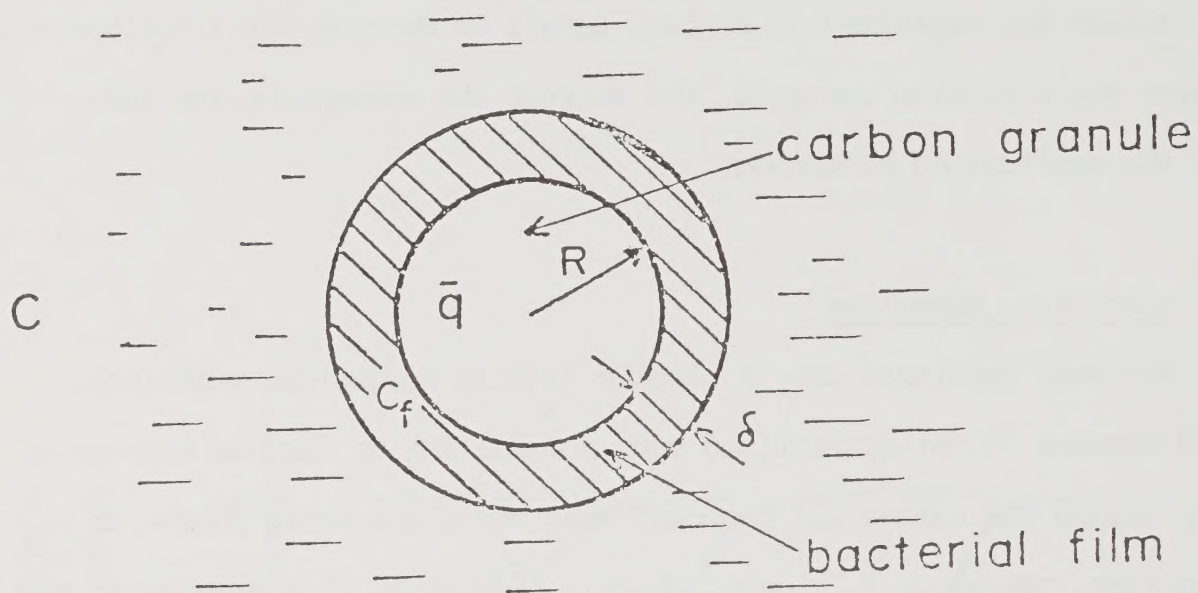
δ = bacterial film thickness,

$\bar{q}$ = average solute concentration - in solid phase,

C = bulk solute concentration, and

Z = bed depth.

FIGURE I-2.7. (FROM PEEL AND BENEDEK, 1975)



An Activated Carbon Granule

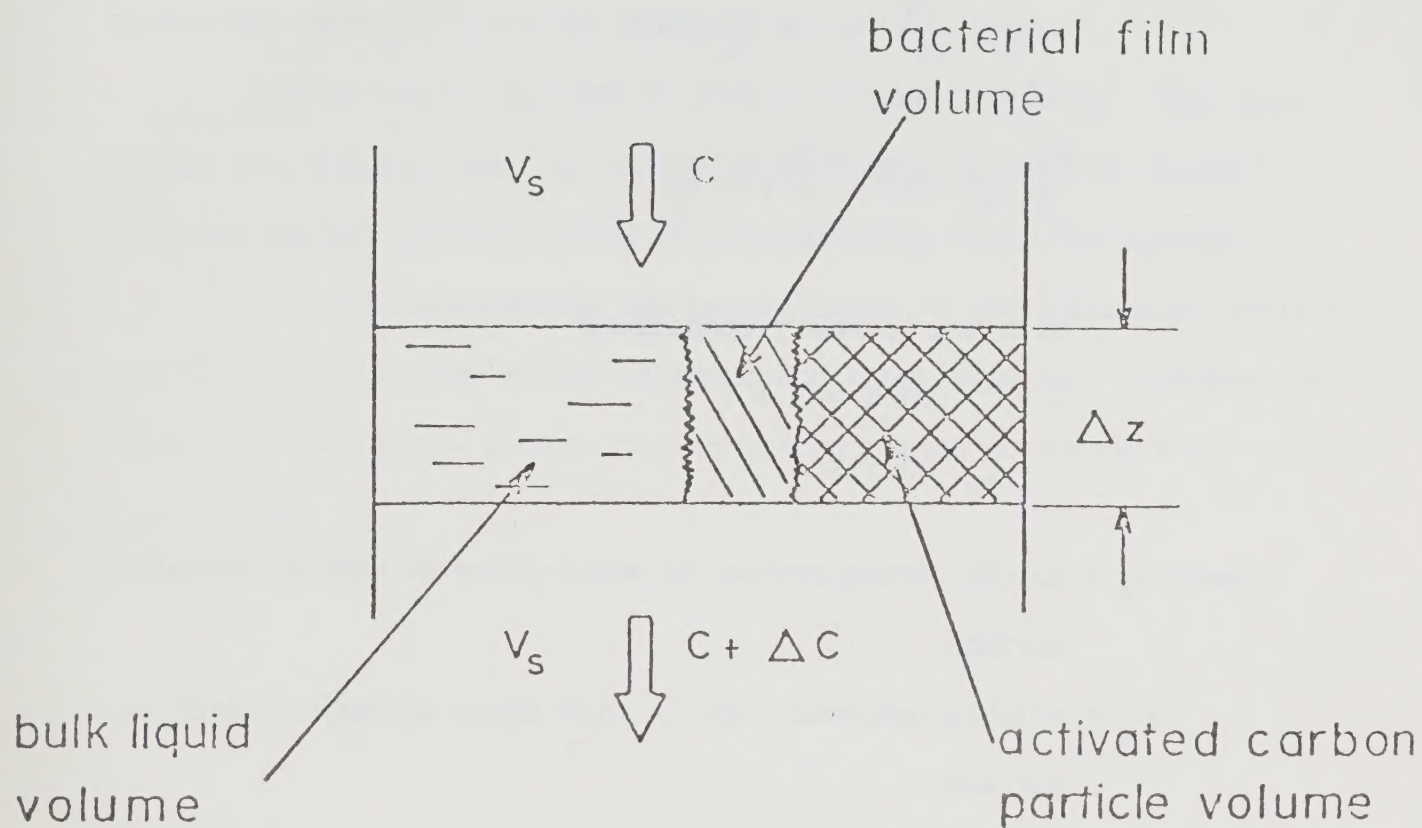
δ = bacterial film thickness

R = carbon granule radius

C_f = solute concentration in the film

$\bar{q}$ = average solute concentration in solid phase.

FIGURE I-2.8. (FROM PEEL AND BENEDEK, 1975)



An Adsorber Segment

V_s = superficial column velocity

C = degradable solute concentration

ΔZ = incremental bed depth

ΔC = change in C over Z

with additional equations of

$$q_s = (C_s),$$

$$a_p (-D_f \cdot \frac{\partial C_f}{\partial r} / R) = k_p a_p (q_s - \bar{q})$$

$$- D_f \cdot \frac{\partial C_f}{\partial r} / R + = k_L (C^+ - C)$$

$$\frac{D_f}{r^2} \frac{\partial}{\partial r} (r^2 \cdot \frac{\partial C}{\partial r}) = R_f$$

with the boundary conditions

$$C = C^+ \text{ at } r = R + \delta$$

$$C = C_s \text{ at } r = R$$

where q_s = solute concentration in solid phase at carbon particle surface,

C_s = soluble concentration in film phase at carbon particle surface,

a_p = bacterial film interfacial area per unit volume,

D_f = solute diffusivity in film phase,

r = radial position in bacterial film,

k_p = intraparticle mass transfer coefficient,

k_L = liquid film mass transfer coefficient, and

C^+ = solute concentration at outer surface of bacterial film.

Numerical solution of the above equations will yield adsorber effluent concentration as a function of adsorbate properties (from isotherm and kinetics), feed flow rate and carbon properties.

I-2.7 SUMMARY

Activated carbon is a highly porous non-specific adsorbent capable of adsorbing a wide variety of organics. The less soluble or polar substrate the greater is its adsorptivity and, in the case of ionizable compounds, changes in pH can strongly affect adsorption.

Carbon can be applied in powder or granular form. For high carbon use applications, as in the case of general organic removal, granular carbon is most likely the economically preferred option.

A carbon application can be evaluated in the laboratory through laboratory tests such as the isotherm and kinetic tests. Mathematical models are available for predicting the operating performance of granular carbon beds.

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II ACTIVATED CARBON ADSORPTION IN WATER TREATMENT

II-1 THE TECHNOLOGY OF CURRENT WATER TREATMENT PRACTICE

As already indicated at the beginning of Section I-2, activated carbon is the only adsorbent of commercial importance in water treatment. There are several thousand plants using activated carbon in the industrialized world for (i) dechlorination, and (ii) taste and odour removal. Most of the dechlorination plants are operated by private concerns (e.g., breweries, soft drink makers) and in addition to dechlorination, some improvement of organoleptic qualities are also accomplished in such cases. Taste and odour removal at municipal plants have been traditionally attained by the use of powdered carbon. Recently, however, several factors developed that favour granular carbon applications; these are:

- (i) higher carbon dosages necessitated by the worsening organoleptic quality of raw surface waters,
- (ii) improvement in commercial granular carbon properties and cost (vis a vis powdered carbon), and
- (iii) concern with general organic removal beyond simple taste and odour reduction.

As a result, granular carbon adsorbers have been placed into service all over the world. In Canada, the first plant designed with activated carbon in mind has come on stream in 1977 at Deseronto, Ont. and two plants in the prairie provinces are experimenting with activated carbon in one of their former sand filters.

In the United States, the number of plants subjecting all their water to activated carbon were listed by Symons (1976) as 33; an additional 13 plants were listed to provide partial treatment. In all

North American plants, the treatment objective is taste and odour removal.

In Western Europe, particularly in Germany, France and Switzerland, most of the larger plants have either been built to include, have been already converted or are expected to be converted to granular carbon treatment. In Germany, there are some 50 plants now converted; mostly along the Rhine and many of the plants along the Rhine are concerned with general organic removal as well as taste and odour control. In Switzerland and Sweden, the main concern is safety (in case of an industrial organic spill) while taste and odour and general organic removal are considered secondary in importance.

II-1.1 Adsorber Location

The flow diagram of a traditional water treatment plant is shown in Figure II-1.1. Raw water is usually breakpoint chlorinated immediately at the intake. Subsequently alum is added as coagulant and powdered activated carbon (PAC) may be added for taste and odour removal. The coagulated colloids may be flocculated separately, ahead of the clarifier, or within the clarifier (in the case of solid-contact clarifier). The settled, water is usually polished in gravity, rapid sand, filters and after post-chlorination, sent to the distribution network.

Initially, activated carbon was introduced into the rapid sand filters by replacing a portion or all of the sand with carbon.

Recently, faced with the concern for longer useful carbon life, newer plants have often been built with two or more filtration stages; first sand then carbon. An example of such a plant is the Morsang-sur-Seine, France plant (see Figure II-1.2). This plant has many interesting features

FIGURE II-1.1.1. CONVENTIONAL NORTH AMERICAN WATER TREATMENT PLANT LAYOUT

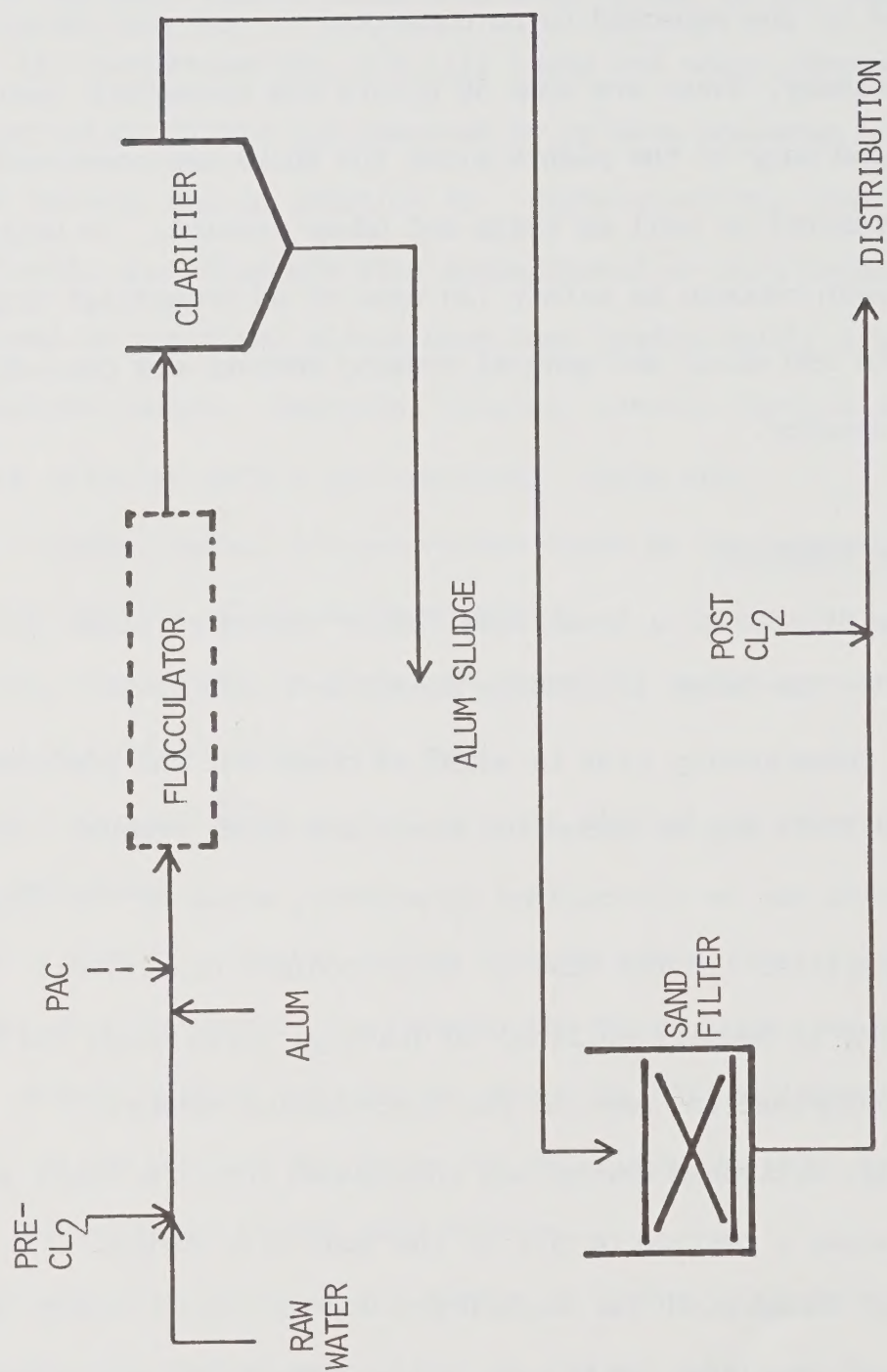
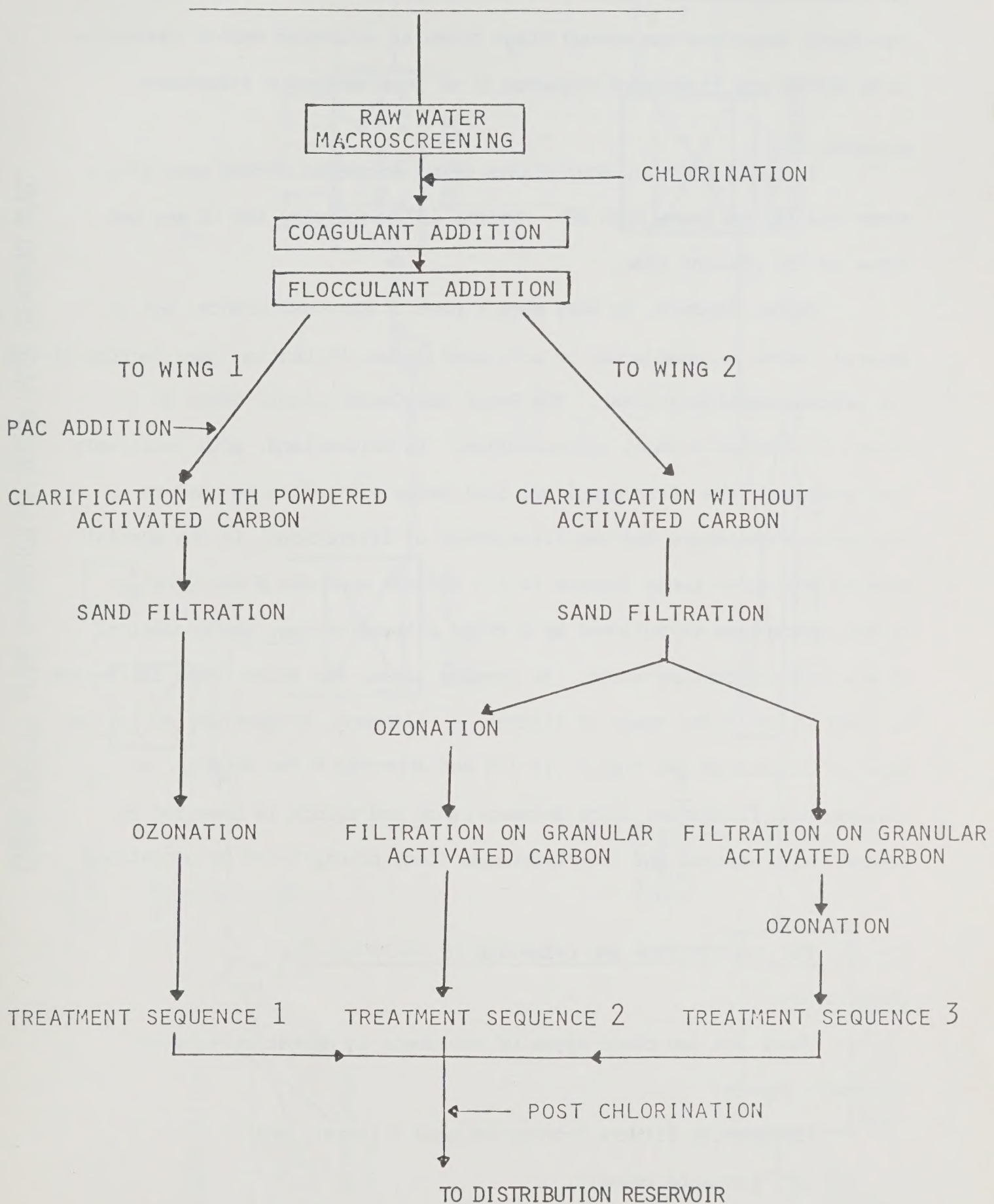


FIGURE II-1.2. TREATMENT SCHEMATICS OF THE MORSANG WATER TREATMENT PLANT



and offers in one plant three different treatment sequences. The first treatment sequence is traditional (as described earlier) while the other treatment sequences use second stage granular activated carbon adsorption with either pre (treatment sequence 2) or post ozonation (treatment sequence 3).

In North America, most plants using activated carbon have single stage filtration (more than 80% Symons, 1977) and very few if any use ozone at the present time.

Ozone, however, is very much a part of European plants, and in general, ozone is used prior to activated carbon filtration (see Section II-2.1 for process considerations). The Swiss and German plants often go to direct filtration without sedimentation. In Switzerland, with relatively low turbidity lake water supplies, dual media filtration is used to replace sedimentation and the first stage of filtration. In the special case of Zürich or Lengg (Figure II-1.3 and see Appendix B for details) carbon adsorption is followed by a third filtration step, the biological or slow sand filtration stage. In Germany, along the Rhine, bank filtration is used as the first stage of filtration, although, frequently, as in the case of Dusseldorf (see Figure II-1.4 and Appendix B for details) an intermediate filtration stage between ozone and carbon is inserted to remove the manganese and iron hydroxide flocs precipitated by ozonation.

II-1.2 THE CONSTRUCTION AND OPERATION OF ADSORBERS

Construction

There are two basic types of adsorbers in operation at water treatment plants:

- (i) gravity filters (converted sand filters), and
- (ii) pressure vessels.

FIGURE II-1.3. PLANT SCHEMATICS FOR ZÜRICH WATER TREATMENT PLANT

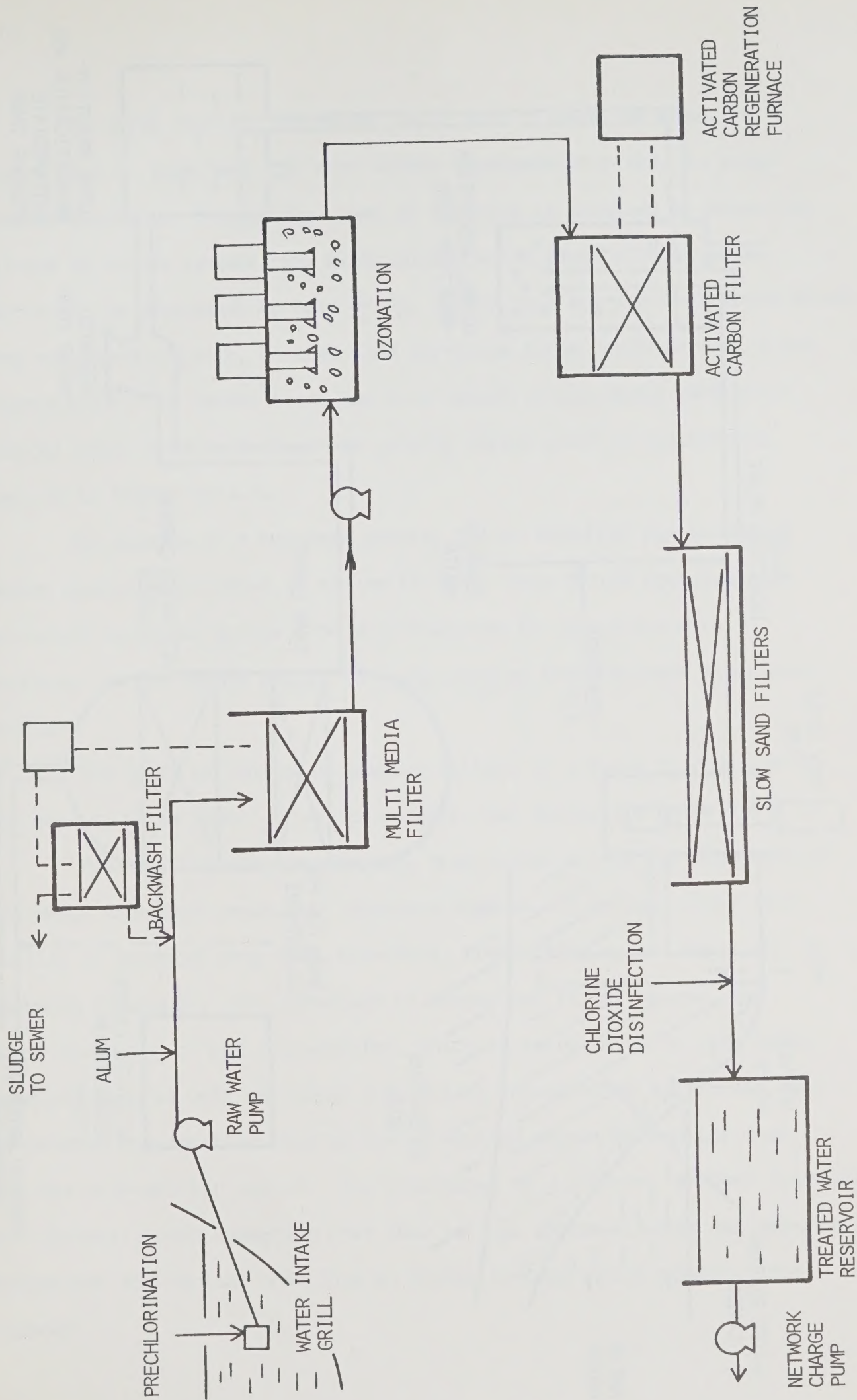
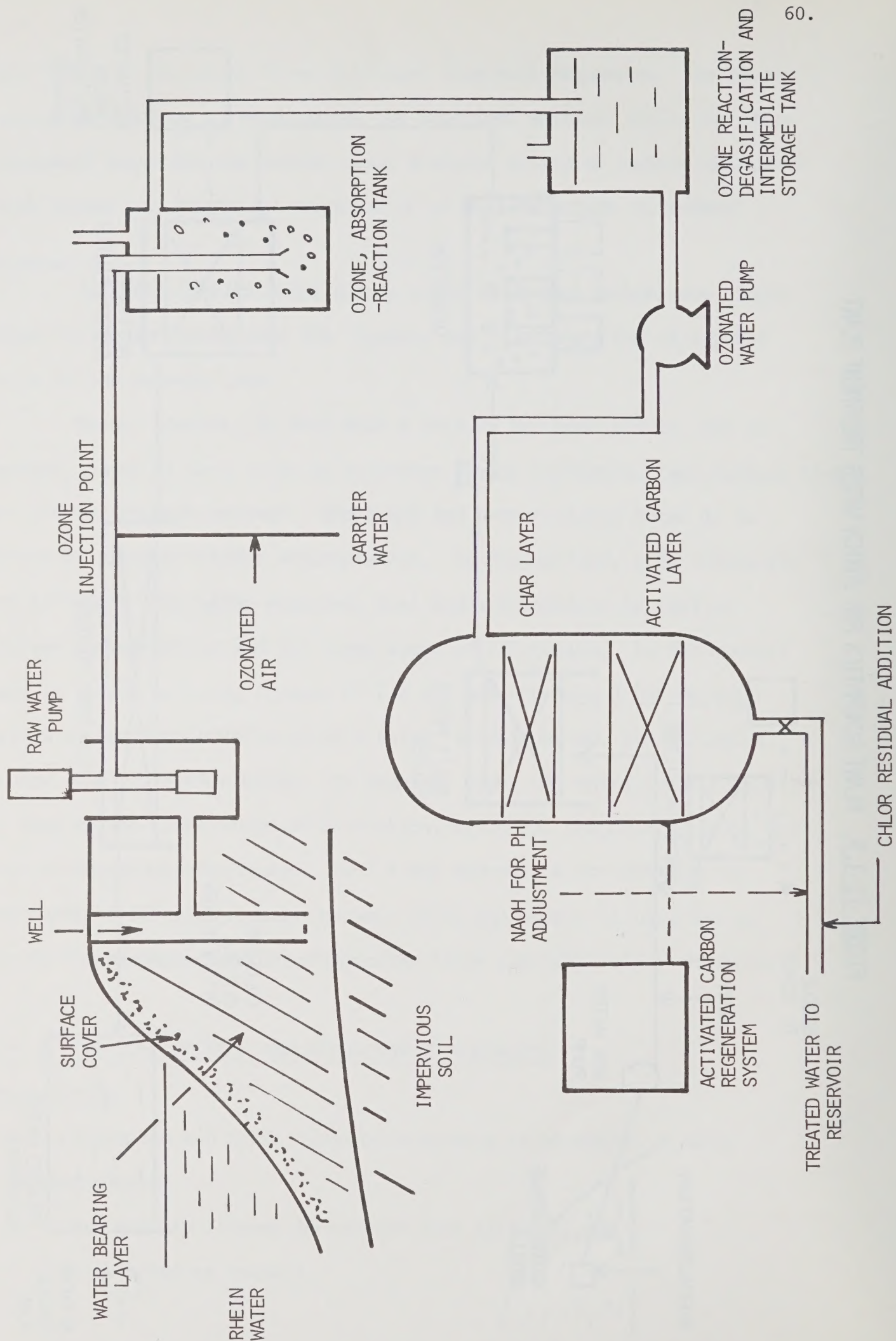


FIGURE II-1.4. PLANT SCHEMATICS FOR DUSSELDORF WATER TREATMENT PLANT



In North America, converted rapid sand filters, as shown in Figure II-1.5, have been the most common arrangement to date in water treatment plants. Frequently, some of the sand is retained in converted filters to insure proper flow distribution and a final filtration of bacteria. As discussed by Love et al. (1975), this has not been found necessary and, particularly, because sand particles cause problems during bed regeneration, the recent trend has been toward single media (activated carbon) only. Gravity filters are usually constructed of concrete as implied in Figure II-1.5.

An example of a European gravity filter modified for activated carbon operation is shown in Figure II-1.6. This filter contains only activated carbon as medium. The modifications for operation with activated carbon relate mainly to needs arising from backwash associated problems.

The depth of carbon in gravity filters is limited by the size of the gravity water head. Thus, in general, bed depths are below 1.5 m.

Pressure vessels are the more traditional method for adsorbers in non-water treatment practice. Pressure vessels, of course, offer flexibility in pressure drop and, therefore, flexibility in bed depth and backwash frequency. The advantage of deeper bed is, of course, the lower frequency of bed regeneration, which in turns saves on both carbon handling cost as well as carbon loss during regeneration and in the case of on-site regeneration (due to lower required capacity) capital cost for the regeneration system. The advantages of a reduced backwash frequency are similar; both operating cost (due to less backwash water and operator attention) and capital cost (due to higher average plant capacity) are reduced.

FIGURE 11-1.5. (FROM HANSEN, 1975)

TYPICAL EXAMPLE OF CONVERSION OF SAND FILTERS
TO GRANULAR CARBON FILTERS.

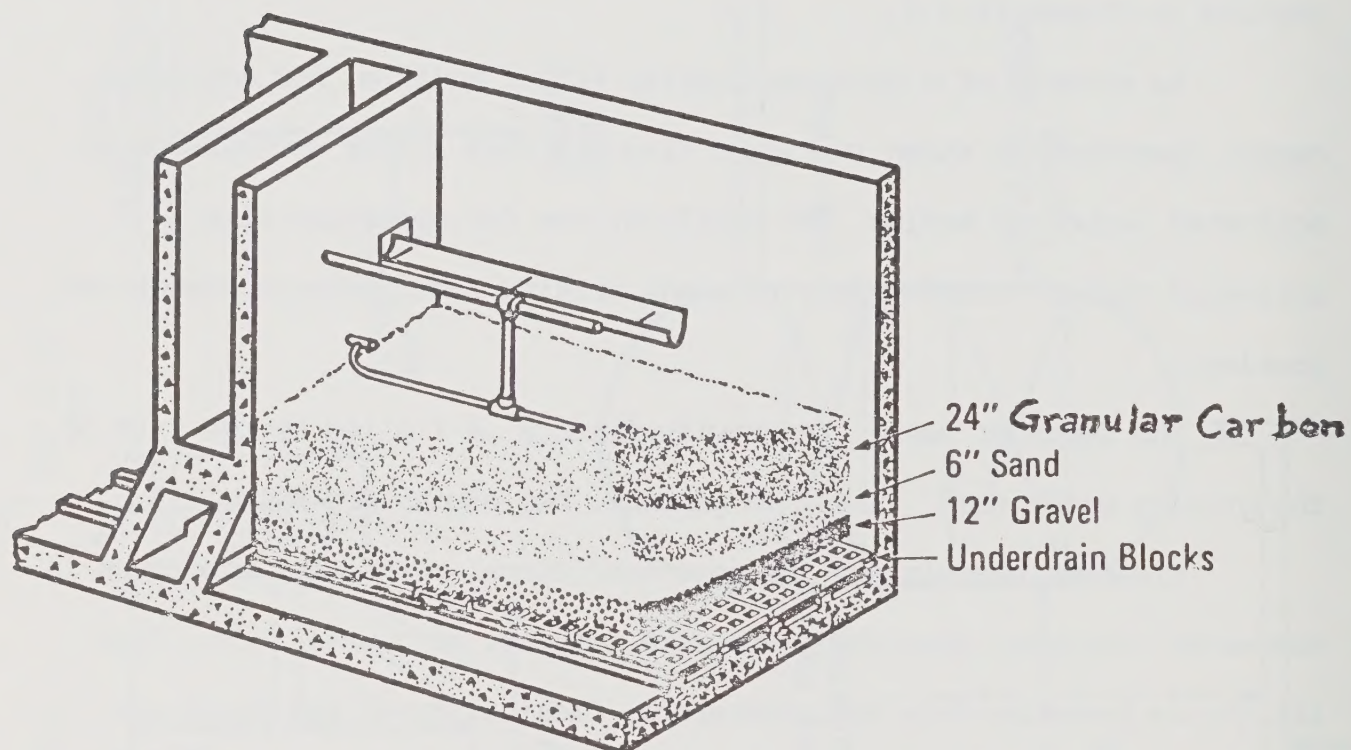
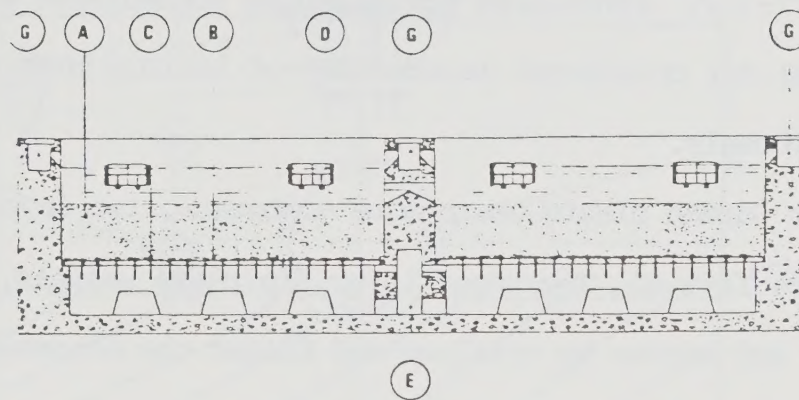


FIGURE II-1.6. MORSANG CARBON FILTERS



— Model 'T' AQUAZUR dual filter with concrete floor and air water channel.

- | | |
|------------------------------|--|
| A. Sand. | E. Air water distribution and filtered water outlet channel. |
| B. Concrete floor. | G. Sludge extraction channels. |
| C. Nozzles. | |
| D. Water inlet clack-valves. | |

Pressure vessels are usually constructed of steel, lined or coated with a water impervious substance for the prevention of corrosion. A disadvantage of steel vessels over concrete basins is that the cross-sectional area of such filters (particularly those prefabricated) is limited and, hence, the capital cost for the auxiliary equipment associated with the filters tends to be higher. Furthermore, due to the cylindrical shape of each filter, pressure vessels are not area efficient.

An example of a pressure vessel in water treatment service is shown in Figure II-1.7. Provisions for bleeding accumulated air and openings (manhole) for occasional maintenance of linings must be provided on all pressure vessels.

Some West German plants use a more elaborate, two layer pressure vessel (see Figure II-1.8). The upper layer, in these vessels, contains unactivated char and serves to catalyze and filter the manganese and iron hydroxides whose precipitation is initiated during the preozonation stage. These vessels tend to be quite complicated as they usually provide for separate air/water backwash of each layer.

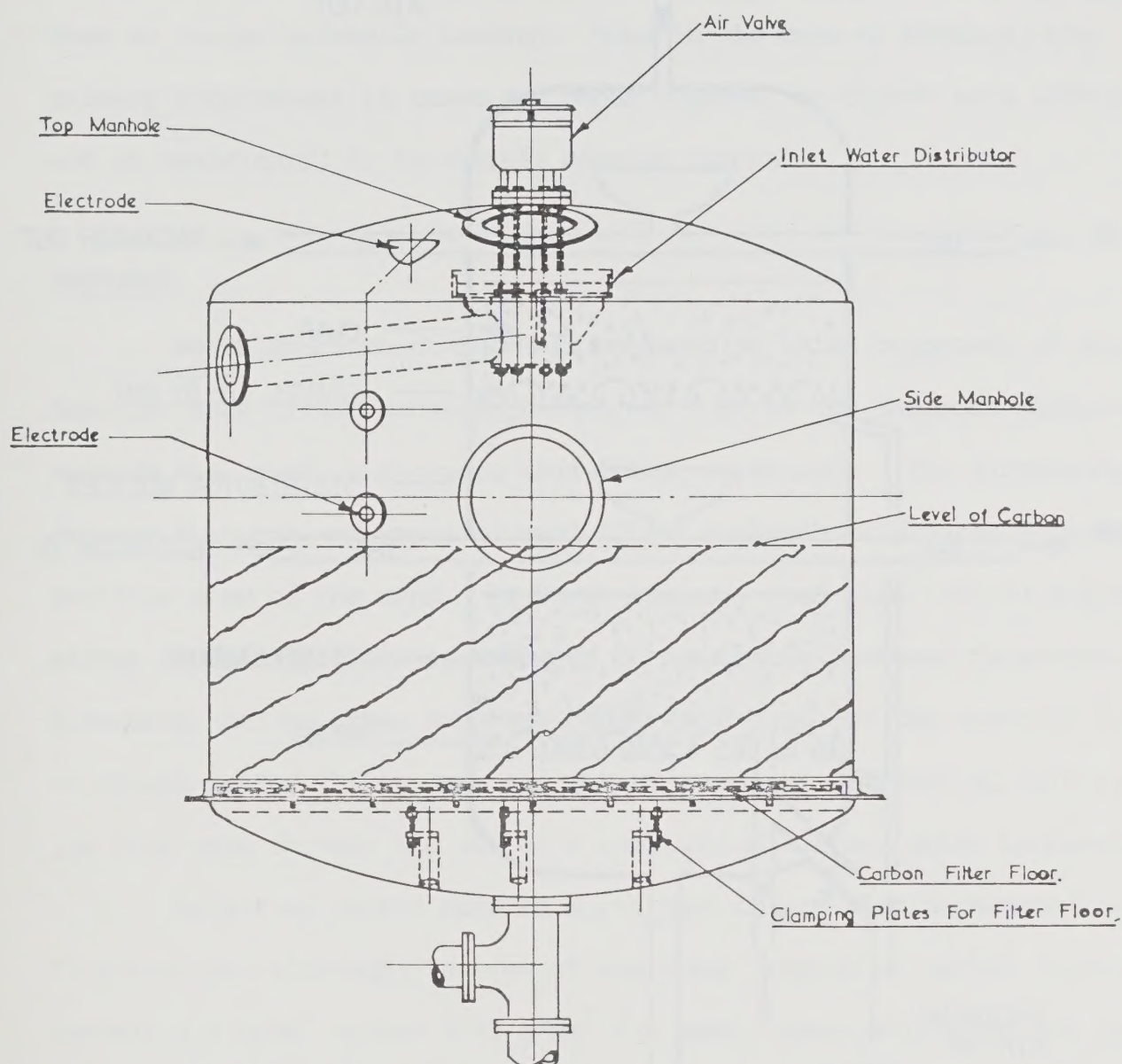
Hydraulic Loading

During normal operation, the hydraulic loading tends to be a function of pretreatment and bed depth; higher level of pretreatment and deeper beds normally allow higher hydraulic loadings.

In North American practice, the applied hydraulic loading is usually at or close to 5 m/h (Symons, 1976). This would be similar to European plants with carbon in the first stage. With carbon in the second stage, however, much higher hydraulic loadings are used, e.g., Morsang, Zürich and Dusseldorf use design average loadings of 16.5 m/h,

FIGURE II-1.7. PRESSURE VESSEL UTILIZED AS A CARBON FILTER

(FROM FORD, 1974)

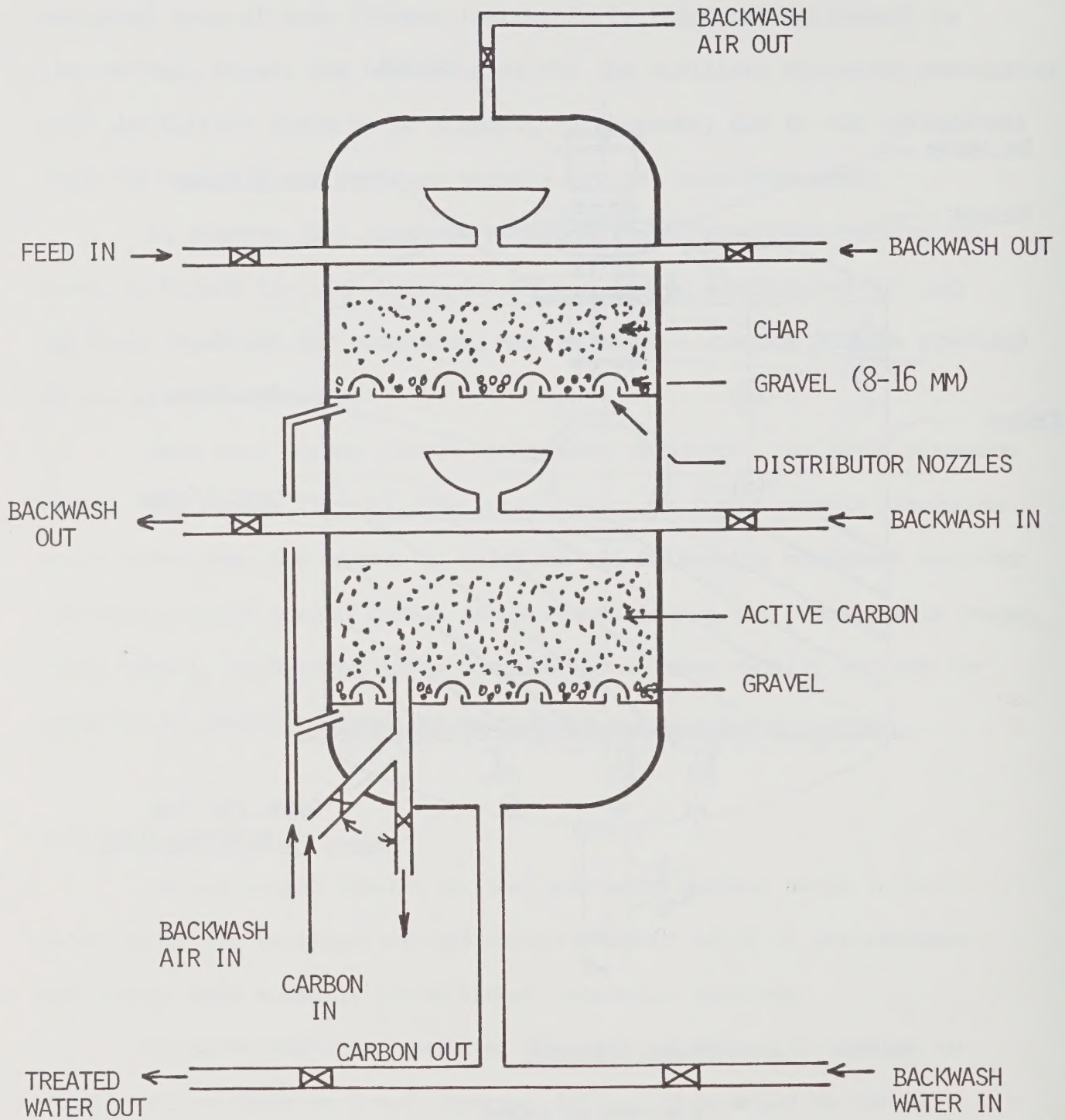


Front Elevation.

3 No. TANKS AS SHOWN.

3 No. TANKS OTHER HAND.

FIGURE II-1.8. DÜSSELDORF ACTIVATED CARBON FILTER



24 m/h, and 9 m/h respectively. The relatively low, 9 m/h, at Dusseldorf (Holthausen) is also allowed to rise, on occasions, to a maximum of 21 m/h. Interestingly, the bed depth used at these three plants are 1.3 m, 0.7 m, and 2.5 m respectively and the differences in bed depth in these cases are more connected to the purpose of the adsorption stage than to design hydraulic loading. Thus in the case of Morsang, the primary requirement is taste and odour control, at Zürich it's safety and at Dusseldorf, it is overall organic removal.

Backwash

North American practice in backwashing is an outgrowth of North American sand filter backwash techniques just as the European backwash methods are based on European sand filter experience. The difference between European and American sand filter backwash originates from the particle size of the sand. In North America, sand size (around 0.6 mm) allows fluidization during backwash at reasonable backwash flowrates. Europeans, on the other hand use larger sand size (on the order of 1 mm) to obtain longer filter runs and obtain excellent backwash at relatively low flow rate through the use of a combination air and water backwash.

Activated carbon beds in North America are also backwashed by fluidization, although, in view of the lower density of carbon (approximately 1.4 g/cm^3 versus 2.65 g/cm^3 for sand) lower velocities are used. This, in turn, results in particle scouring which may or not be sufficient, depending on the qualities of the pretreated water (alum flocs on excessive biological growth, for example, may cause carbon particles to bind). In such cases, in America, a surface wash system, is used. Approximately half of the plants in North America use surface wash (Symons, 1976), a relatively costly operation (see Section II-1.3).

Europeans, on the other hand, tend to use, in the main, an initial air scour followed by a water rinse. The Degremont company in conjunction with Societe Lyonnaise des Eaux et de l'Eclairage experimented for many years to develop a suitable air/water backwash system and details of their system is given in Appendix B. One important aspect of their system is the special filter modifications needed for avoiding bursts of air during rinsing and for bleeding air during operation. Air bursts are a problem during the initial start up phase of the water rinse that immediately follows air backwash. Air bursts are now avoided by the design of the air/water inlet nozzle and by the lowering of initial water level (prior to air backwash). Once the filter is back into operation, the residual air from backwash as well as the air released from the water under the lower pressure at the effluent collector level, are continuously bled by a separate air bleed line.

A strong advantage of backwash by water fluidization alone is low loss of carbon through attrition. From pilot experiments, Nemeth (1976) concluded that such losses could become considerable with air wash. On the basis of these experiments, the adsorbers at Gothenburg are washed with water only to 30% expansion in 2 minutes. Subsequently, the released flocs are washed out of the adsorber by the opening of a short side wall (of the rectangular adsorber/filter) to drain cross flow water admitted at the opposite side wall.

In the case of Gothenburg (carbon in the first stage) the above described backwash, without surface wash, appears to be completely adequate for backwash purposes. The loss of carbon due to backwash based attrition is claimed to be on the order of only 1%. On the other hand, over a three year period, with proper operation of an air/water backwash system Fessinger (1977) in an almost identical plant, at Viry-Chatillon (near

Paris), found a similar (0.9%) loss of carbon in 3 years of operation. Fiessinger credits this low loss to the control of air bursts as described above as well as the controlled backwash conditions (which are similar to those given for Morsang-sur-Seine in Appendix B).

Carbon Regeneration

Carbon regeneration or reactivation is a process wherein an exhausted carbon is made to regain a significant proportion of its original activity. There are two basic methods of carbon regeneration, namely, solvent or thermal reactivation. Solvent regeneration has been attempted recently by the Degremont Co., France, and independently, by the Engler Bunte Institute for Water Chemistry, Germany. Unfortunately residual solvent taste and odour problems are difficult to eliminate and, therefore, solvent regeneration is unlikely to make in-roads in water treatment, although, in other areas, this method of regeneration still appears to have potential.

Thermal reactivation is the only commercially viable method today. It leaves no residual taste and odour. It generally restores close to virgin capacity the exhausted water treatment carbons and there are no residues emitted to the environment during regeneration or on subsequent return to service. The major disadvantage of thermal regeneration is high capital cost.

Due to this high capital cost and low regeneration frequency, exhausted water treatment carbons in North America are either not regenerated or are regenerated by carbon manufacturers on a custom basis. Only Nitro, West Virginia, had ever installed an on site regeneration system, however, this system due to change in water supply

is no longer in use.

In Europe, on the other hand, five on site regeneration systems have been built in view of the high organic content of many rivers used for water supplies coupled to the desire to achieve a very high organic treatment level. There are two multiple hearth furnace based systems in operation. The flow diagram for the Gothenburg system is shown in Figure II-1.9. Carbon is transported from the adsorbers/filters to a spent carbon tank. Carbon is then educted to a dewatering screw which, in turn, feeds the carbon to the top hearth of the furnace. As carbon passes down, along each of the six hearths of the furnace, it is first dried then reactivated (by pyrolysis) and finally cooled. Typically the pyrolysis hearths, 4 and 5, are usually between 850-1,000 °C. Subsequently, the carbon is quenched, stored in the regenerated carbon tank and returned, as needed to the adsorbers.

The multiple hearth furnace is the most widely used furnace in America for carbon regeneration due to its relatively low cost (at high throughput) mechanical ruggedness and efficient use of heat. On the other hand, multiple hearth furnaces are hard to start-up or shut-down and are, therefore, not well suited to the low throughput and on and off type operation desired at water treatment plants.

A fluidized bed furnace appears to overcome this advantage and recently fluid-bed furnaces were installed at three water treatment plants, each manufactured by a different company. In a fluid bed regeneration system, only the furnace and its associated equipment is different from the multiple hearth system described earlier.

The schematics of the fluid bed furnace at Zürich is shown in Figure II-1.10. The furnace itself consists of a single stage hearth on which an upward flow of combustion gases fluidize the horizontally

FIGURE 11-1.9.

PROCESS FLOW SHEET FOR CARBON REGENERATION AT THE GOTHENBURG, SWEDEN WATER TREATMENT PLANT
(COURTESY OF THE HUMPHREY AND GLASGOW, LONDON)

M-101
DEWATERING
SCREW

F-101

CARBON REGENERATION
FURNACE

T-101
FOULLED CARBON TANK

M-103
CARBON
EDUCTOR

EXISTING GRAVITY
FILTERS

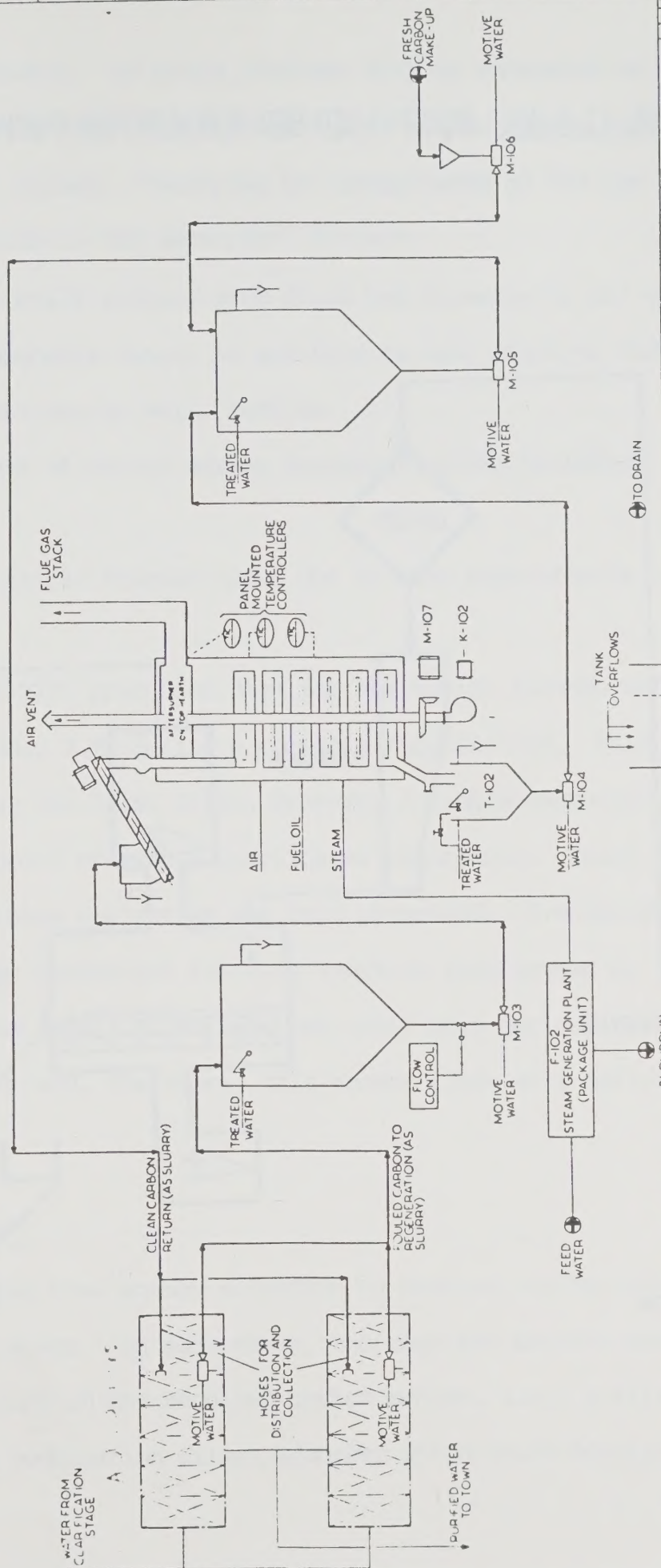
T-102
QUENCH TANK

M-104
CARBON
EDUCTOR

T-103
CLEAN CARBON TANK

M-105
CARBON
EDUCTOR

M-106
CARBON EDUCTOR
(MAKE-UP)



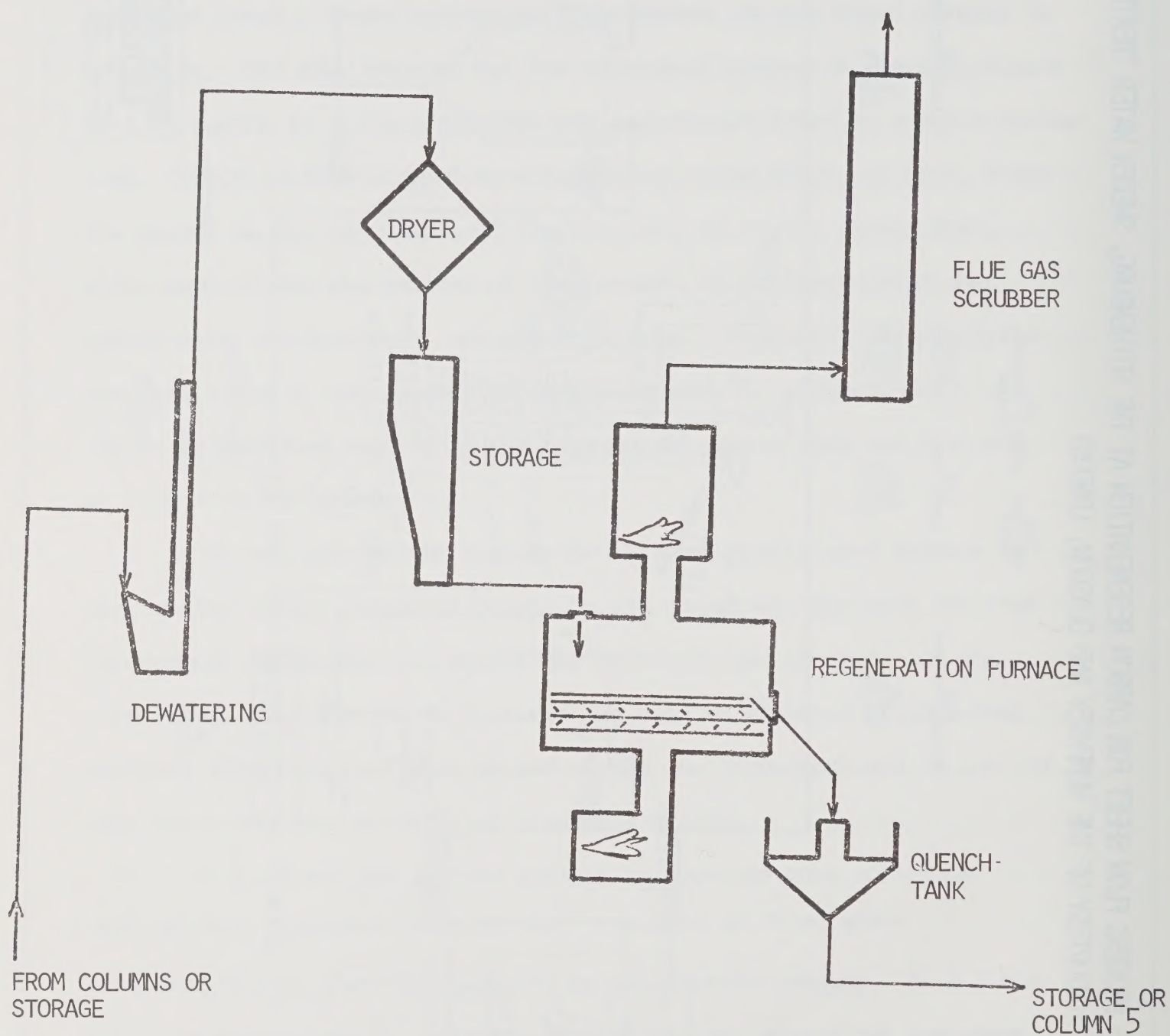
HUMPHREYS & GLASGOW
LONDON - STONEY - TORONTO - BOMBAE
PLANT CARBON REGENERATION PLANT
CLIENT LOCATION GOTHENBURG WATER-TREATMENT PLANT

T-105
COLLECTION
PIT

BLOWDOWN

HUMPHREYS & GLASGOW
LONDON - STONEY - TORONTO - BOMBAE

FIGURE II-1.10. NORIT FLUID BED REGENERATION FURNACE AT THE ZÜRICH PLANT



moving particles of carbon. To avoid problems with an excessive or variable feed moisture content, predrying in a rotating, batch, vacuum dryer is practiced at Zürich. Predrying is accomplished by the use of a second stage or hearth in the Düsseldorf furnace.

Experience is still limited with fluid bed furnaces at all water treatment sites. Proponents claim, in addition to easy start-up and shut down, other advantages as well, such as

(i) lower loss of carbon during regeneration due to better reaction control

(ii) lower particle fragmentation due to less mechanically caused attrition.

Schalenkamp (1977) presented data for the Zürich furnace which indicated a loss of only 3.5% during a complete regeneration. This would tend to bear out the first claim, however, a single regeneration is insufficient for proof of such a complicated phenomenon. Proof for lower attrition rates has not as yet been presented. Eventhough there is little if any mechanical friction (such as that caused by multiple hearth rabble arms), fluid beds can still have serious fluid shear caused attrition and, therefore, this second claim will definitely need to be proven.

II-1.3 Treatment Cost

Presently, the most common situation in America, is the use of carbon in the first stage. In such cases, the required capital cost is essentially the cost of the required carbon medium, i.e., a filter in this case acts as a combination filter/adsorber which would doubtless

have to be built or would have been already built. The saving in cost of the normal sand medium, in the case of a new plant or the expense of sand disposal, in the case of an existing plant can be considered negligible in comparison to the purchase cost of fresh carbon.

Ross (1976) indicates that approximately \$2,000,000 was required for the conversion of existing sand filters and the leasing of carbon (essentially equivalent to custom regeneration) for two plants treating drinking water for 500,000 people. The total quantity of carbon installed in these filters was approximately 970 tonnes. Assuming typical custom regeneration costs of \$0.90/kg and makeup carbon costs of \$1.45 kg (and a split between regenerated and makeup carbon needs after 3 years of 4:1 (a very conservative ratio)), the carbon supply and makeup costs are calculated to be approximately \$1,000,000. The remaining \$1,000,000 are associated with initial conversion costs which include:

- (i) labour associated with emptying and refilling of beds,
- (ii) disposal costs for sand,
- (iii) improved filter instrumentation,
- (iv) painting of steel surfaces to avoid corrosion, and
- (v) engineering and contingency.

The installation of surface wash can be quite expensive. Ross (1976) estimated such costs as \$1,500,000 for plants serving a population of 500,000 people. The need for surface wash, however, has never been established and, in plants employing a satisfactory presedimentation stage, surface wash is probably unnecessary.

Costs for carbon filter backwash are somewhat less than the equivalent costs for sand filters due to lower water use. Nemeth (1977) indicates that at Gothenburg (plant capacity $300,000 \text{ m}^3/\text{d}$) approximately two million m^3 of water were saved annually after conversion to activated carbon.

Operating cost, in this case, can be restricted to the cost of regeneration (probably on a custom basis) of the exhausted carbon and the purchase of make-up carbon as the backwash. Filter instrumentation costs were probably the major cost among the above and this is not always necessary.

Assuming a water requirement of $.4 \text{ m}^3/\text{d}/\text{capita}$, and amortization on capital at 10% over 20 years, the additional cost per m^3 of water to the consumer can be estimated at approximately 0.6¢. In terms of a typical Canadian family using 1.2 m^3 of water per day, carbon adsorption would add \$2.60 to their annual water bill.

In the case of secondary or tertiary stage carbon filtration, costs would be substantially higher as in this case, the entire cost of adsorber construction and operation must be counted. In the case of secondary stage adsorption, two types of costs must be examined, namely, the cost for a taste/odour/safety oriented application and the cost for an overall organic removal oriented application. The Zürich and Düsseldorf plants, respectively, serve as good examples of the above two orientations.

The adsorption stage costs have been listed by Schalenkamp (1975) for Zurich, on the basis of $40,000,000 \text{ m}^3/\text{yr}$ of production, as approximately $\$0.012/\text{m}^3$ of water for the amortization of capital costs and $\$0.004/\text{m}^3$ for operating costs (including the capital costs of the reactivation system). Hence the total cost paid by the consumer for the carbon adsorption stage is $\$0.016/\text{m}^3$ or, approximately, \$7.00 per year for the typical Canadian family using $1.2 \text{ m}^3/\text{d}$ of water.

In the case of Düsseldorf, the city would like to eliminate the

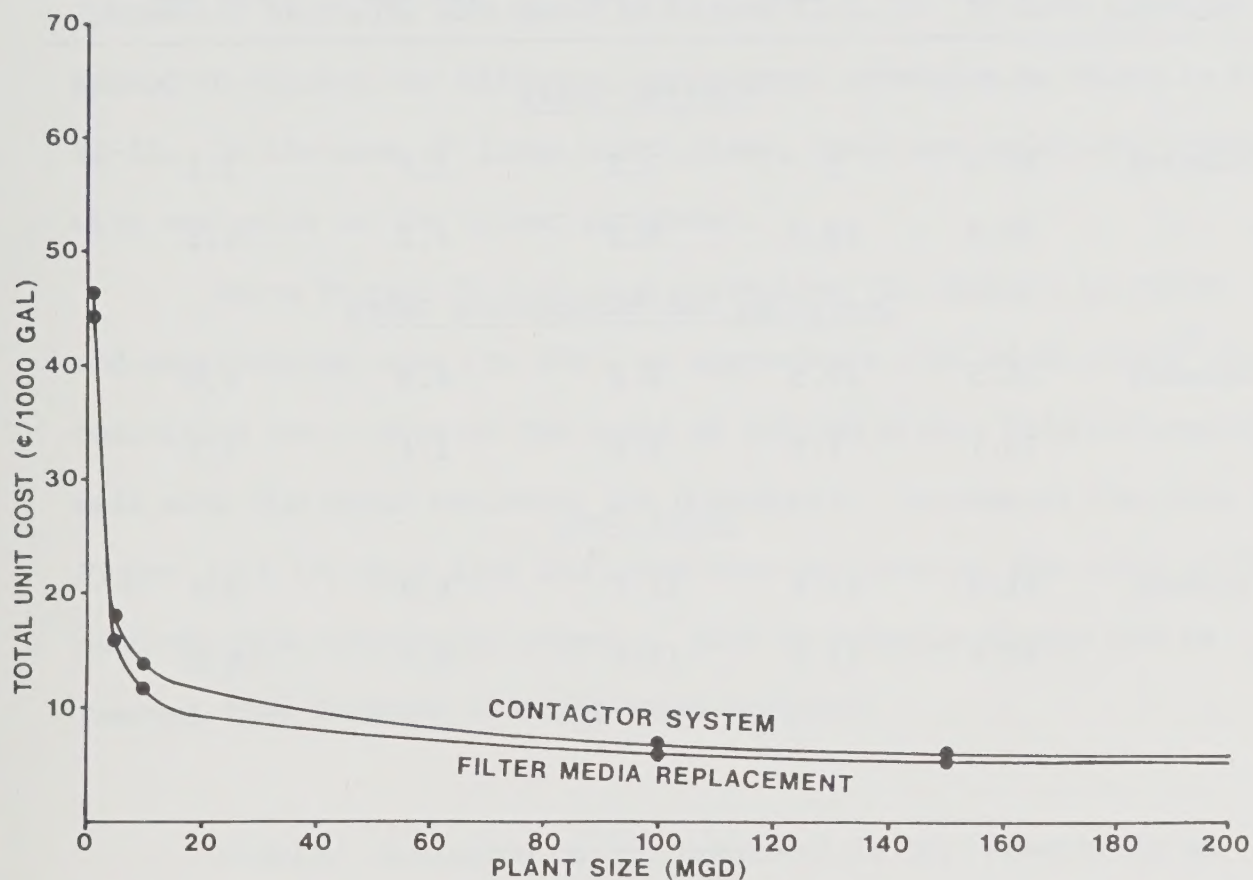
majority of organics from their drinking water. Initially, Düsseldorf replaced carbon at a rate of only 3 g/m^3 , a rate typical of plants using carbon for taste and odour removal only. Subsequently, it raised its replacement rate to 15 g/m^3 and recently, with the commissioning of the reactivation plant, city engineers decided to increase replacement rate to 30 g/m^3 . The cost of the reactivation system, which includes modifications to adsorbers as well as complete automation is given by Poggenburg (1977) as approximately \$2,000,000. Assuming that other costs can be linearly extrapolated from Zurich estimates (on the basis of a 10:1 ratio in carbon replacement rate and a 14% payback rate), a total operating cost of $\$0.027/\text{m}^3$ can be calculated.

The above costs are very approximate and are only included to show the actual range of carbon costs encountered at operating plants.

The US EPA (1977) developed cost correlations for the potential use of carbon adsorption in trihalomethane removal. As trihalomethanes breakthrough rapidly (see Section II-2.5), their correlations were based on a 1.4 month carbon replacement time. Other design parameters were representative of those commonly encountered (see Section II-1.2).

The summary curves for the first and second stage application are shown in Figure II-1.11. On the basis of this figure, there appears to be little difference between first and second stage systems in view of the higher operating costs of first stage systems (see Table II-1.1).

FIGURE II-1.11. CARBON ADSORPTION COST CURVES AS A FUNCTION OF PLANT SIZE (FROM US EPA, 1977). MEDIA REPLACEMENT IS EQUIVALENT TO FIRST STAGE AND SEPARATE CONTACTOR IS EQUIVALENT TO SECOND STAGE ADSORBERS IN TERMS OF THE NOMENCLATURE OF THIS REPORT.



Comparison of Costs between Contactor System and Media Replacement versus Plant Capacity.

TABLE II-1.1. CAPITAL AND O&M COSTS FOR GRANULAR CARBON ADSORBERS
WITH ON-SITE REACTIVATION (FROM US EPA, 1977)

(¢/1000 gal.)

System	1 mgd	5 mgd	10 mgd	100 mgd	150 mgd
<u>Capital Costs</u>					
Media Replacement	21.5	5	3.5	1.5	1.1
Contactors	30.2	10.2	8.2	4.3	4.1
<u>Operating and Maintenance Costs</u>					
Media Replacement	21.5	10.5	8.2	4.5	4.0
Contactors	16.1	7.3	5.4	2.4	2.2
<u>Total Cost</u>					
Media Replacement	41.0	15.5	11.7	6.0	5.1
Contactors	46.3	17.5	13.6	6.7	6.3

The higher operating cost of the first stage system is based on higher carbon losses, however, in view of the discussion in Section II-1.2, this may not be the case. The variable costs in this model such as carbon cost (assumed to be \$0.38/lb), amortization rate (assumed to be 7%) tend to be low by present standards. Fortunately, the report provides methods of correction for variations in such costs, e.g., the set of curves suggested for correcting O&M costs for carbon cost changes (presently \$0.65/lb) are shown in Figure II-1.12. It also provides a method to correct for different replacement schedules as shown in Figure II-1.13. In the case of large plant sizes, costs are relatively stable with variation in the latter parameter.

Using Figure II-1.11, and correcting for changes in carbon cost and amortization rate (to 10%), an approximate cost of \$0.033/m³ can be calculated for plants on the order of 120,000 m³/d. This corresponds well with the costs estimated for Düsseldorf. In view of the data in Figure II-1.13, this also indicates that at costs on the order of \$17/yr, even the less adsorbable organics, such as trihalomethanes can be removed from Canadian drinking water supplies.

Finally, activated carbon treatment is not necessarily an expense item, provided that design engineers are willing to look at the treatment system as a whole. Thus Keller et al. (1974) estimate that for the case of a coloured but non-turbid water (a common situation in Canada), a combination ozone and activated carbon treatment scheme is cheaper than the conventional coagulation, sedimentation and sand filtration alternative.

FIGURE II-1.12. THE EFFECT OF CHANGES IN VIRGIN CARBON COST (\$0.38 ASSUMED IN TABLE II-1.1) ON ADSORBER O&M COST (FROM US EPA, 1977).

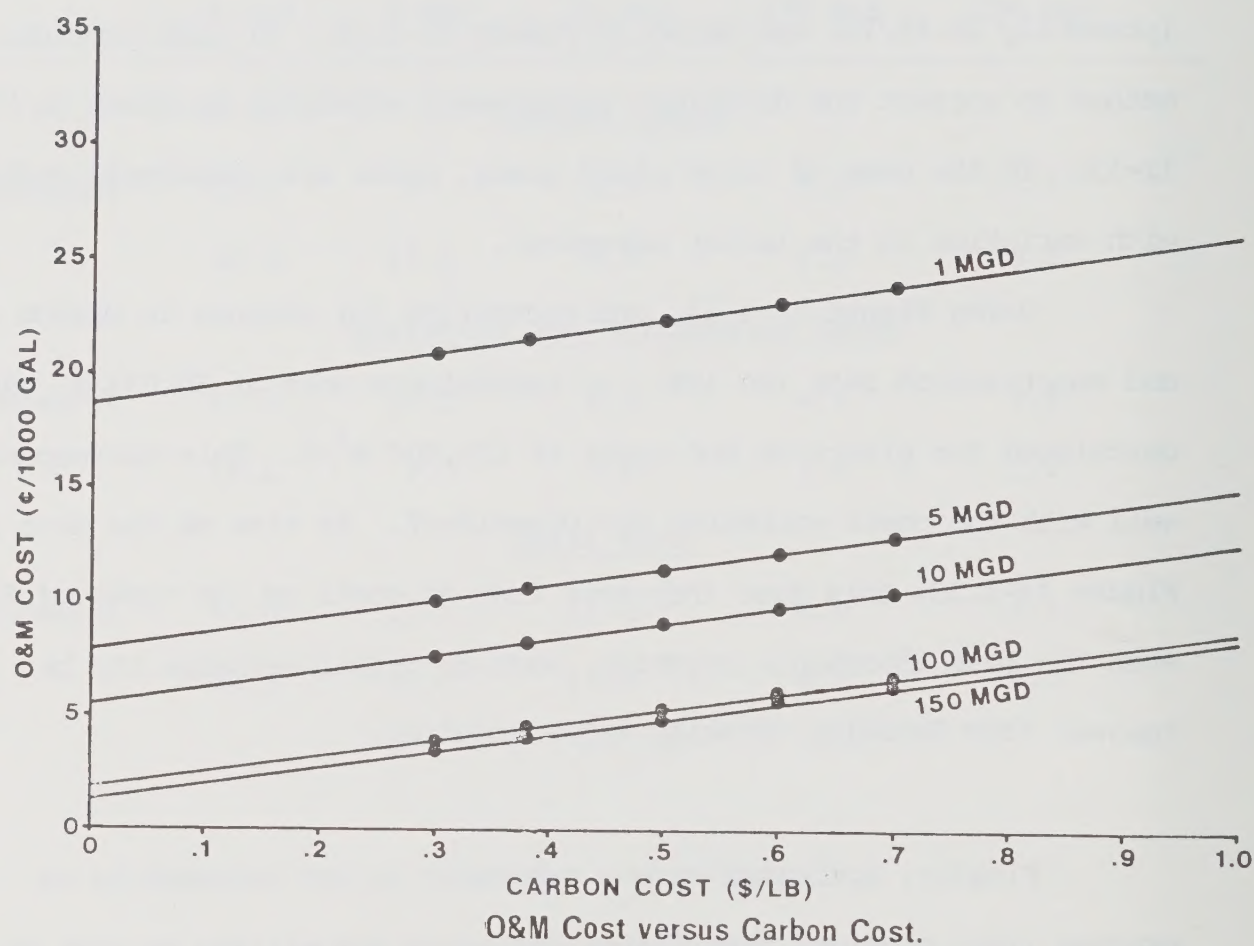
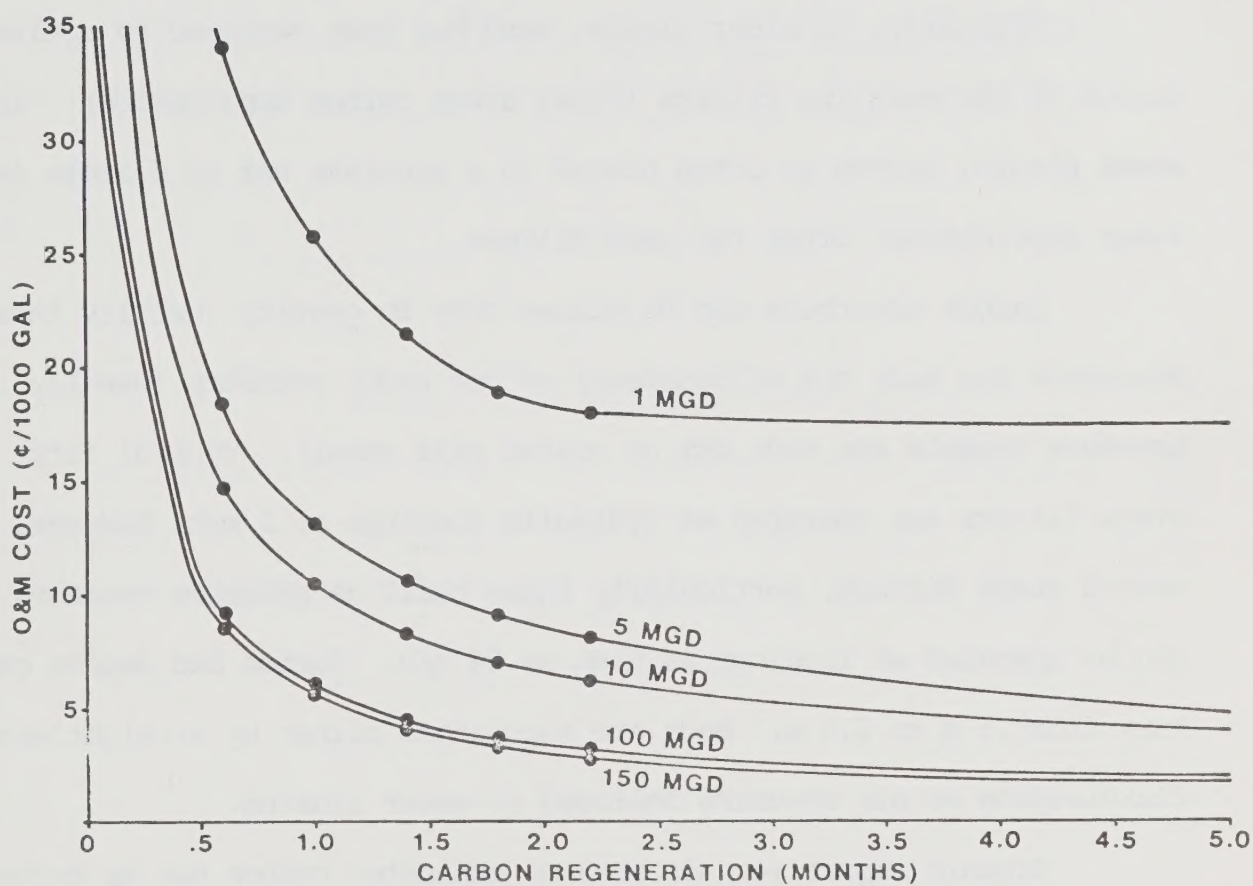


FIGURE II-1.13. THE EFFECT OF CHANGES IN CARBON REPLACEMENT SCHEDULE (1.4 MONTHS ASSUMED IN TABLE II-1.1 (FROM US EPA, 1977))



O&M Cost versus Regeneration Frequency.

II-1.4. SUMMARY

Activated carbon applications have been increasing around the world in recent years in view of increasing problems with taste and odour as well as concern for general organic removal. The concern for organic removal is particularly important in some western European countries and, in some cases, safety from industrial organic spills has also been a reason for employing granular activated carbon adsorbers.

Typically, in older plants, sand has been replaced by activated carbon in the existing filters (first stage carbon application). In newer plants, carbon is often placed in a separate set of filters (second stage application) after the sand filters.

Carbon adsorbers can be either open to gravity (usually these adsorbers are made out of concrete) or put under pressure (usually pressure vessels are made out of coated mild steel). Typical first stage filters are operated at hydraulic loadings of 5 m/h, however, second stage filters, particularly those built as pressure vessels, can be operated at loadings as high as 24 m/h. Carbon bed depths can vary from .5 m to 2.5 m. Beds are backwashed either by straight water fluidization or air scouring followed by water rinsing.

Organic impurities adsorbed on exhausted carbon can be burned to CO_2 and thus reactivated carbon can be returned to service. There are five water treatment plants in Western Europe with on-site reactivation furnaces; three of the plants use fluidized bed furnaces, a promising new type of furnace. Other plants, usually send their exhausted carbon back to manufacturers for reactivation.

The additional cost of treatment for carbon adsorption at low level carbon use (for taste and odour) would be on the order of \$2/yr (for first stage) to \$17/yr (second stage), for a Canadian family using

1.2 m³/d of water. If general organics removals are desired, costs could rise to \$20/yr for this same family. It is probable, however, that by redesigning treatment plants on a total system basis, the cost would be less than the above.

II-1.5 REFERENCES

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II-2 PROCESS ASPECTS OF ACTIVATED CARBON ADSORPTION IN WATER TREATMENT

This chapter attempts to explain the reasons behind the design variables listed in Chapter II-1. In addition, it focusses on the capability of current potable water treatment plants for the removal of organics.

II-2.1 Pretreatment

As discussed in Section II-1.1, carbon adsorption usually follows prechlorination and coagulation and sometimes sand filtration and/or ozonation.

Prechlorination if deemed necessary for other than organic removal reasons tends to improve adsorption. Chlorination, in general, is believed to result in less polar hence more adsorbable organics (Hassler, 1963) and in the case of a particularly important group of organics, phenols, Gauntlett and Packham (1975) demonstrated remarkable improvements in adsorptivity on chlorination. On the other hand, chlorination can also result in molecular fragmentation and the formation of halomethanes (as discussed in Section I-1.1.4) and halomethanes are not well adsorbed by carbon (see Section II-2.5). Thus, wherever possible, prechlorination should be avoided.

Proper coagulation can remove as much as 60% of the organics present in raw water (Fiessinger, 1976). Most of these organics are in colloidal or particulate form although depending on raw water quality, much of the removed organics can be humic acids.

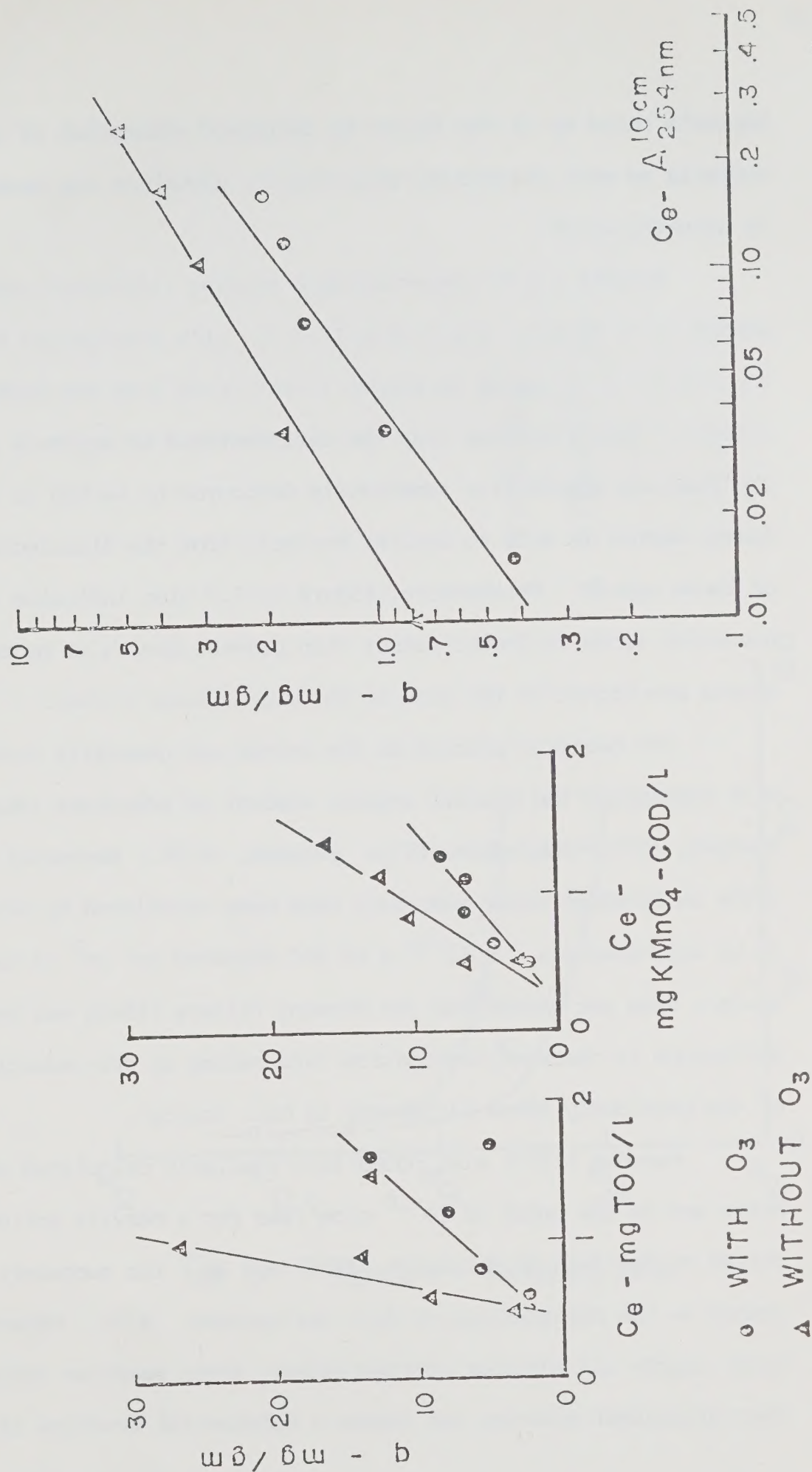
Sand filtration has little if any effect on soluble organics (when pre-chlorination is practiced). Its main effect on carbon adsorption occurs through the reduction in carbon operating cost as prefiltration allows the use of finer carbon particles, reduces carbon loss through attrition in view of fewer backwashes (see Section II-1.4).

Finally, ozonation reduces the adsorptivity of organics by increasing the number of polar groups (hence increasing solubility) along the molecular chains. The effect of ozonation was clearly demonstrated by Benedek (1977) who showed remarkably lower adsorptivities after ozonation (see Figure II-2.1. On the other hand, ozonation is believed to improve biological activity and, as shown in the section below, this tends to make up for the decrease in adsorptivity. Benedek (1977) suggests that from an organic removal standpoint, ozonation should follow adsorption if short carbon replacement schedules are used. In the case of carbon replacement schedules beyond one year, however, pre-ozonation is more advantageous.

II-2.2 Biological Effects

Normally, pre-disinfected water is administered to a freshly installed carbon filter. As pre-disinfection typically leaves a few bacteria (say 1-10 bacteria/ml) in the water, these bacteria immediately adsorb on the carbon. In recently completed unpublished studies, for example, the Société Lyonnaise des Eaux at de l'Eclairage at Le Pecq, France found that after only one day of operation, there are already 10^5 bacteria/g of carbon in an adsorber initially filled with almost bacteria free regenerated carbon. As operation continues,

FIGURE II-2.1.1. MORSANG ISOTHERMS IN TERMS OF A) TOC, B) COD-KMnO₄ AND C) OPTICAL DENSITY (O CARBON EQUILIBRIUM LOADING AND C_E EQUILIBRIUM LIQUID CONCENTRATIONS) (FROM BENEDEK, 1977)



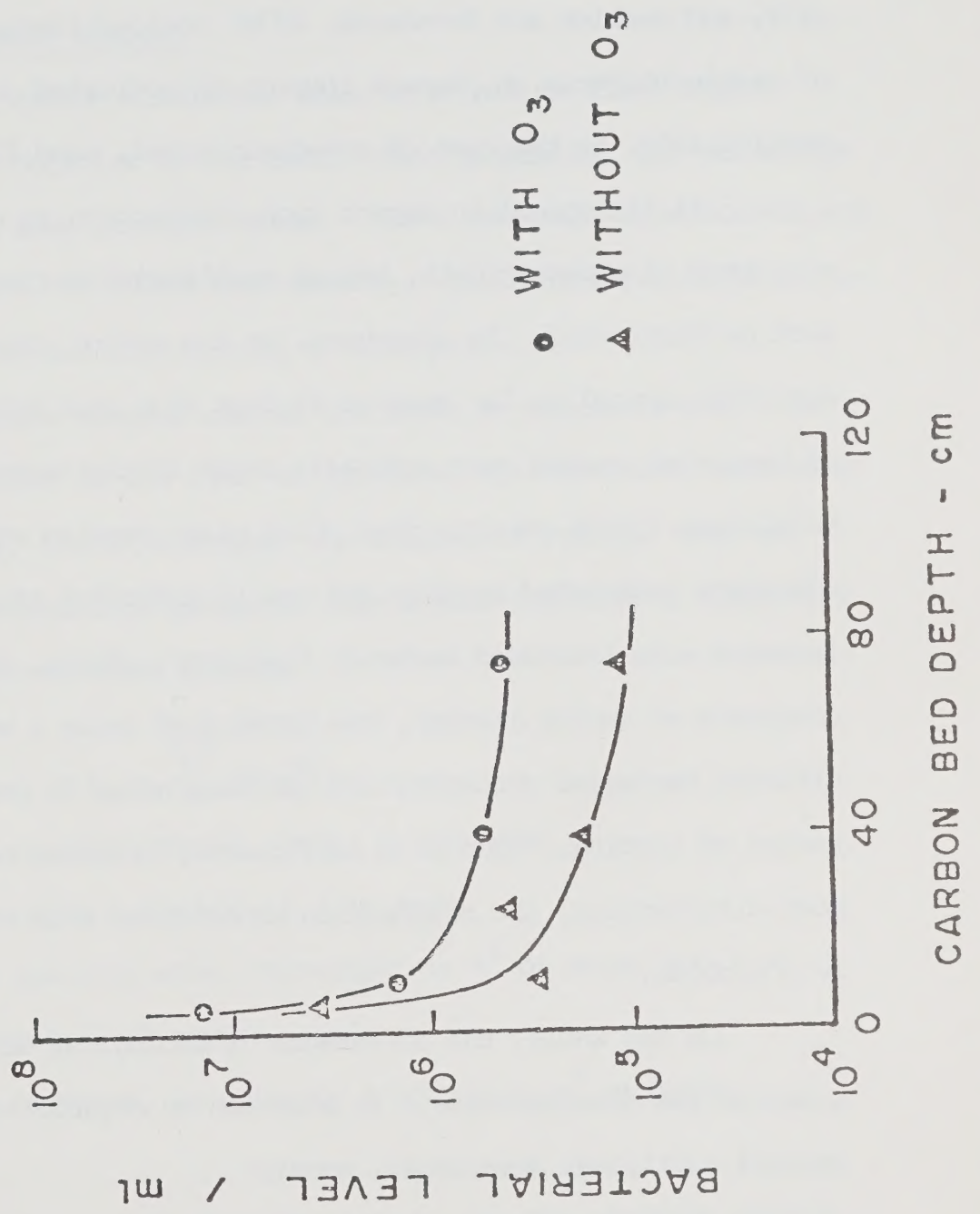
bacteria build up in the filter by continued adsorption of incoming bacteria as well as through heterotrophic growth on the organics found in drinking water.

Benedek (1977) presented data showing viable cell counts in the adsorbers at Morsang (see Figure II-2.2). It's interesting to note that the highest cell counts in Figure II-2.2 occur near the surface of the filters. This indicates that the disinfectants or oxidants present in the feed are essentially immediately destroyed by carbon or that, at least, carbon is able to shelter bacteria from the disinfecting action of these agents. Furthermore, Figure II-2.2 also indicates that pre-ozonation tends to foster rather than prevent growth as bacterial cell counts are higher in the case of the pre-ozonated filter.

The bacteria present on the carbon are generally credited with increasing the overall organic removal of adsorbers (Magsood and Benedek, 1977; Eberhardt, 1975; Benedek, 1977). Bacterial reaction rates on drinking water adsorbers have been calculated by Benedek (1977) to be approximately 2×10^{-11} g of TOC degraded per cm^2 of carbon particle surface area per second for the Morsang filters (there was very little difference in observed degradation rate caused by pre-ozonation in spite of the previously noted difference in cell counts).

Benedek (1977) also noted that similarly calculated degradation rates are on the order of 10^{-10} g/ cm^2 /sec for a heavily polluted river (based on the data of Eberhardt, 1975) and 10^{-9} for secondary effluent (based on the calculations of Peel and Benedek, 1976). Depending on water supply and adsorber configurations, these reaction rates indicate that biological activity can remove a substantial fraction of the applied

FIGURE II-2.2.1. VIABLE CELL COUNTS AT MORSANG (FROM BENEDEK, 1977)



organics, e.g., the Morsang filters are generally removing about 30% of the feed organics.

The presence of bacteria in a potable water treatment adsorber is, of course, a hygienic problem. Many investigators (e.g., Wallis, 1974, and Bueller and Bernhardt, 1976) noticed increases in concentration of viable bacteria on passage through an activated carbon adsorber, particularly, in the case of pre-disinfected, sand filtered, feed.

It is logical to expect such reinfection in biologically active adsorbers as excess growth, beyond equilibrium surface adsorption levels, must be eliminated. In adsorbers, in the second stage, where backwashes are often spaced as far away as 40 days from each other, the elimination of bacterial growth must naturally occur during normal operation. Schalekamp (1975) reports that pilot plant results with parallel adsorbers backwashed monthly and weekly indicated that reinfection is lessened with increased backwash frequency. Hence, the full scale adsorbers at Zürich (Lengg), are backwashed twice a week and the maximum effluent bacterial concentration has been below 50 per ml over a six month period of testing. Thus with sufficiently frequent backwashing coupled to post-disinfection, the reinfection experienced with adsorbers should not be a problem.

On the whole, the advantages of biological activity greatly outweigh its disadvantages. In addition to organic removal, there are several additional advantages, namely:

- i) removal of ammonia, if present, by nitrification to nitrate, and
- ii) transferring the occurrence of potential bacterial growth on the organics present in the water, from distribution lines to the adsorber. Bacterial growth in the distribution lines are

hard to control and require large initial chlorine residuals.

Finally, it must be noted that it is impossible to prevent growth in carbon beds, therefore, we might as well allow it to occur.

II-2.3 Overall Organic Removal

In general, carbon adsorbers, when first put on line, remove close to 90% of the organics in the feed. Then gradually, the percentage removal declines to some constant value. This constant value corresponds to the percent removal attained biologically. The difference between the constant value and actual corresponds to adsorption.

Typical organic removal curves are shown in Figure II-2.3. The data as shown in Figure II-2.3 fits an empirical equation that, according to Poggenburg et al. (1976), describes the decline of removal from the initial value. The equation indicates that a semi-log plot of operating filters will yield a straight line as

$$A_m = \frac{A_o K}{V} (1 - e^{-KV})$$

where A_m = organic removal, in %, at any time t ,

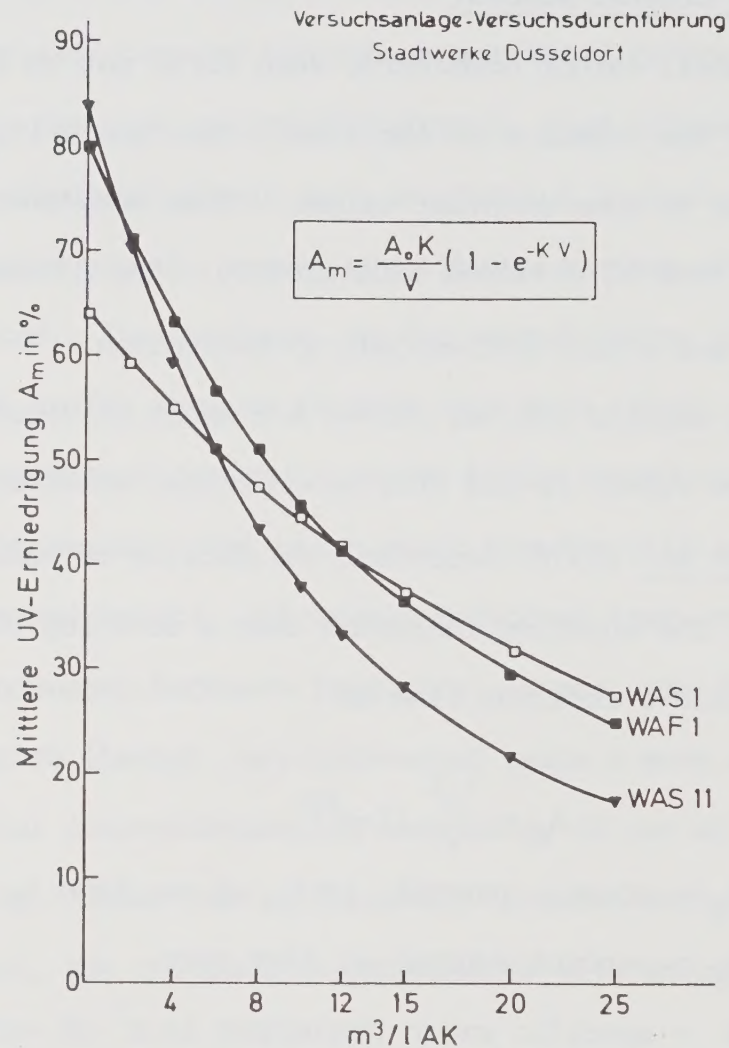
A_o = percent removal at time zero,

V = specific water throughput in m^3 of water per l of activated carbon, and

K = constant, in units of l of carbon/ m^3 of water.

This equation, however, does not take into account the constant removal portion of such curves which have been clearly indicated by other authors (Benedek, 1977; Eberhardt, 1975). This constant removal portion, however, normally does not become observable before 20 m^3 of water (per l of carbon) is passed through an adsorber. The constant slope region, in the

FIGURE II-2.3. ORGANIC REMOVAL IN CARBON ADSORPTION (FROM POGGENBURG ET AL., 1976)



A_m corresponds to UV

Organic Removal (UV absorption base)

AK signifies Activated Carbon and WAS 1, WAF 1 and WAS 2 correspond to the designation of different adsorbers.

case of Morsang has been observed to begin at about $17 \text{ m}^3/\text{l}$ and is still continuing after more than $50 \text{ m}^3/\text{l}$ has passed through the filters.

The average percent organic removal is summarized in Table II-2.1 for the three plants described in detail in Appendix B. The above table is presented simply to show the typical range of organic removals obtained in carbon reactors. In view of the many sided differences between the plants, conclusions are hard to draw, nonetheless, it is interesting to note that the Morsang plant attains removals by biological means which are of the same order of magnitude as the Dusseldorf plant which tends to operate near the point where adsorption still plays a role in organic removal. This difference could be due to the fact that the bank filtrate at Dusseldorf has been already degraded once biologically and, therefore, it is not as readily degradable as the Seine at Morsang.

Design oriented papers are generally lacking. Dostal et al. (1965), in one of the few design oriented studies, showed that the length of effective organic removal (by adsorption) is proportional to contact time or, as they are equivalent for a given adsorber, bed depth. Furthermore, they also noted that decreasing particle size increases effectiveness particularly with regards to odour.

II-2.4 Taste and Odour Compounds

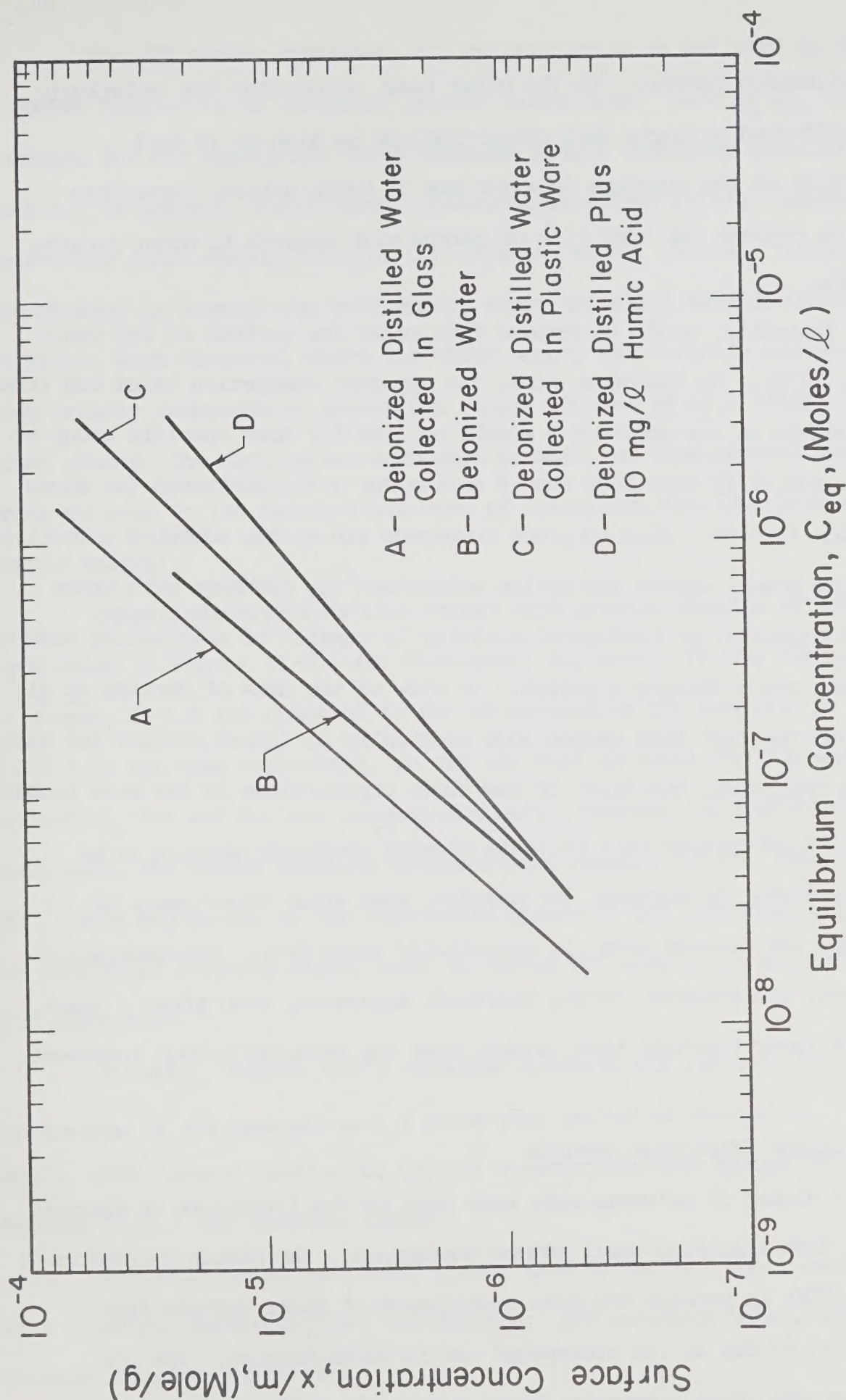
The reduction of taste and odour is the most common reason for utilizing activated carbon in potable water treatment. As discussed in Section I-1.1, 2-exo-hydroxy-2-methyl borneol and geosmin, have been identified as important sources of potable water taste and odour. Laboratory adsorption studies with these compounds are presented by Herzing et al. (1977). They found that the adsorption of these compounds was quite strongly affected by the trace impurities (see Figure II-2.4) leached

TABLE II-2.1

ORGANIC REMOVALS AT THREE EUROPEAN PLANTS

PLANT	PERCENT REMOVAL OBTAINED FROM MEASUREMENTS OF		
	DOC	COD _{KMnO₄}	UV ext.
Düsseldorf (Holthansen)	22	--	40
Morsang (without pre-ozonation)	37	34	--
Zürich (Lengg)	22	18	15

FIGURE 11-2.4. THE EFFECT OF VARIOUS CONTAMINANTS ON ADSORPTIVITY OF MIBK (FROM HERZING ET AL., 1971)



MIB ADSORPTION ISOTHERMS AT pH 5.5 AS A FUNCTION OF THE TYPE OF MAKEUP WATER

from collection vessels. On the other hand, adsorption was relatively little affected by humic acid concentrations as high as 10 mg/l.

As the bulk of the organics in water are of humic nature, these data appear to explain the long life of carbon with regards to odour causing compounds.

Typically, odour is removed from water for periods of 2-5 years (Symons, 1976). On the other hand, the apparent adsorption based bed life for carbon is on the order of 6 months or less for most specific group of organics and it is even less than 6 months for trihalomethanes (as shown in Section II-2.6). Thus odourous compounds are either adsorbed selectively beyond the normal carbon adsorptive exhaustion (by exchange with other adsorbed organics) or biological activity is capable of eliminating some or all of the odour causing organics. In view of the data of Herzing et al. (1977) and the fact that carbon beds eventually do indeed exhaust for these odourous compounds, the first of the above explanations is the more probable.

The exhaustion rate of taste causing compounds appears to be similarly slow. At Morsang, for example, even after three years of operation, the treated water is essentially taste free. Interestingly, at Morsang, the granular carbon treatment sequences, even after 3 years, produce a lower threshold taste number than the powdered carbon treatment sequence.

II-2.5 Carbon Extraction Results

A number of solvents have been used in the literature to extract organics from specified small column contactors. The Carbon Chloroform Extract (CCE) is perhaps the most significant of these methods (see Section I-1.8) due to its widespread use in North America. The CCE number, or any other extraction based number, is difficult to relate to specific groups of organics, or to health effects.

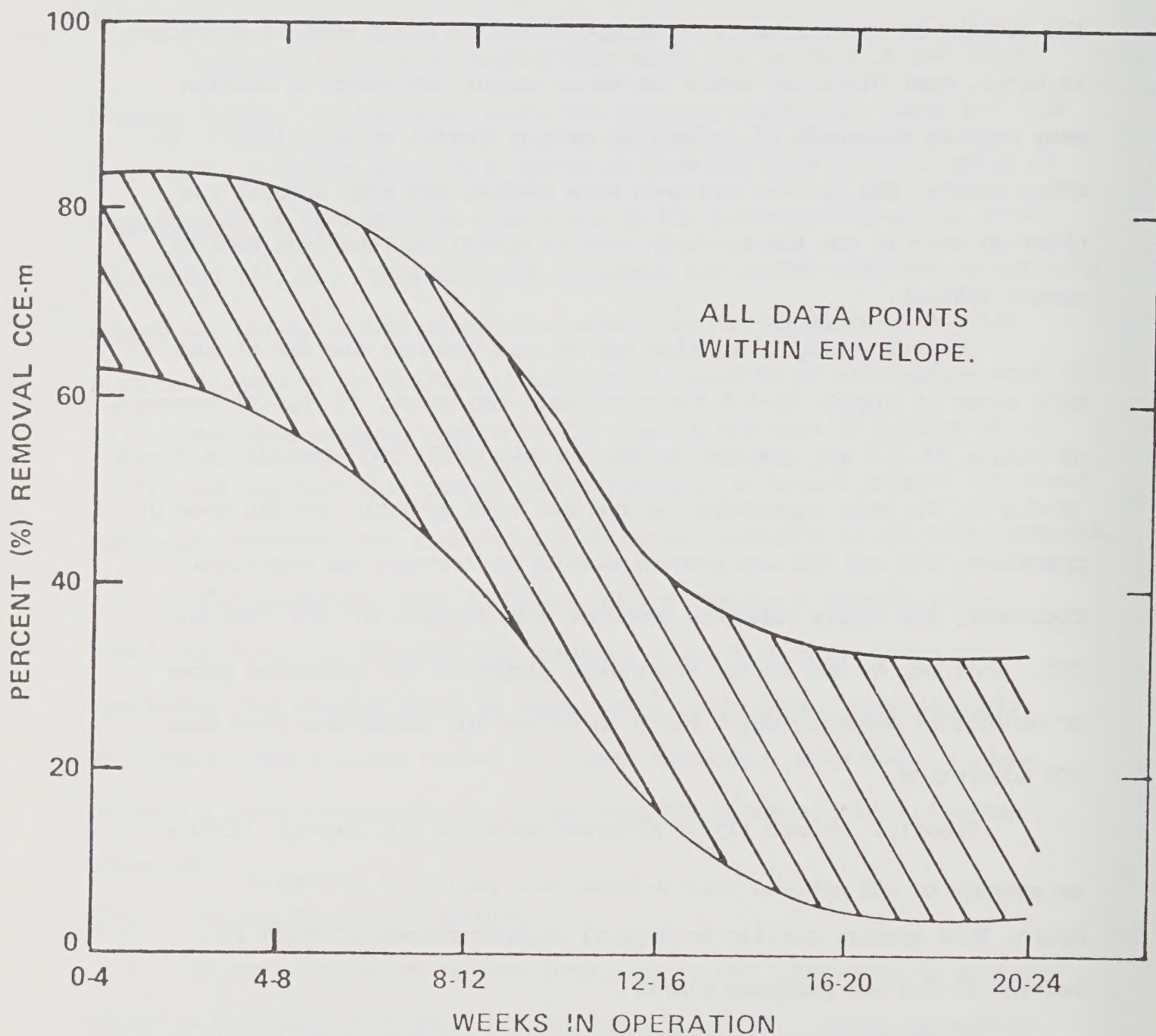
The CCE number expressed as a concentration is believed to be a number indicative of non-polar organic substances. Love et al. (1975) surveyed for CCE adsorption North American plants employing granular carbon. In general, their survey indicated excellent initial removal but relatively short carbon life for CCE organics at all plants. Interestingly, the decline in removal was very abrupt after the sixth week of operation at Nitro, West Virginia, where the water supply was found to contain many organic compounds of industrial origin (Dostal et al., 1965). At other plants, the decline was much more gradual and some removal was observed even in the twenty-sixth week of operation (the last week of sample taking).

Other investigations also report more gradual decline of the type shown in Figure II-2.5 for Cincinnati tap water. If the CCE removals of Figure II-2.5 are compared to the corresponding TOC removals in Figure II-2.6 in the same experiment, we can see that up until the 8th week of operation, CCE and TOC are removed similarly, however, as operation continues, the carbon exhausts somewhat more rapidly for CCE than for TOC. This may be due to the restricted nature of CCE adsorbing pores or biological activity which tends to extend TOC adsorption more than CCE adsorption.

Finally, Hansen (1977) obtained moderate CCE removal listing an average of 22% removal over a three year period of operation. Again, this appears similar to typical organic removals listed in Section II-2.3 for European plants.

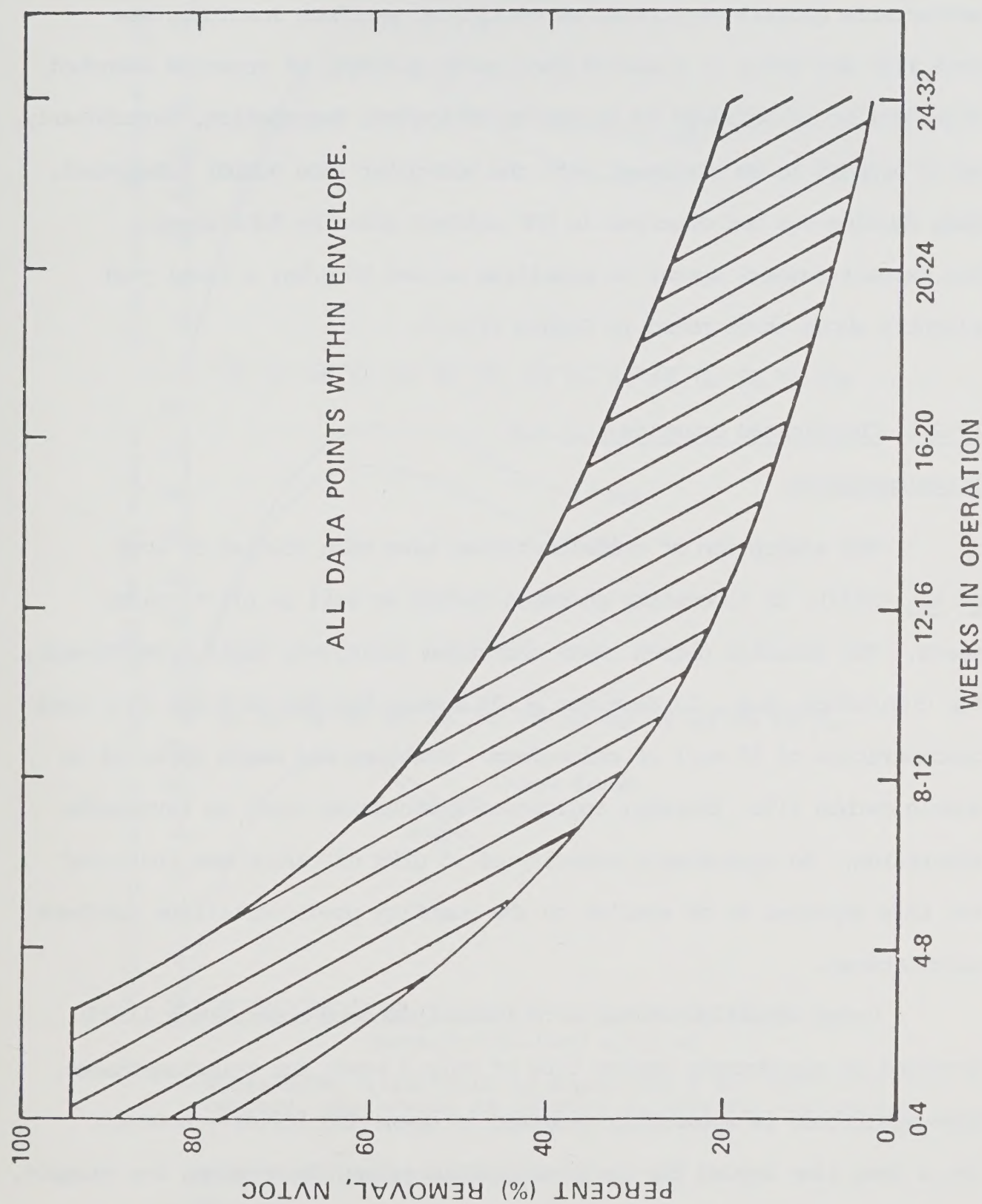
The West German and Swiss plants tend to extract their carbons with dimethyl formamide (DMF) and dioxane. DMF extracts polar, and dioxane nonpolar substances.

FIGURE II-2.5. THE REMOVAL OF CCE MATERIALS BY ACTIVATED CARBON (FROM US EPA, 1975)



CARBON CHLOROFORM EXTRACT (CCE-m) REMOVAL FOR
SIX TYPES OF GRANULAR ACTIVATED CARBON

FIGURE II-2.6. THE REMOVAL OF TOC IN PILOT CARBON COLUMNS (FROM US EPA, 1975)



NON-VOLATILE TOTAL ORGANIC CARBON REMOVAL FOR SIX TYPES
OF GRANULAR ACTIVATED CARBON

Figure II-2.7 shows the quantity of organics extractable by these solvents from water work adsorbers. Interestingly, the maximum extractable quantities correspond to typical isotherm loadings (see Part III) and there is a marked decline on quantity of organics adsorbed. This decline is believed to be due to biological degradation, particularly, as it appears to be strongest with the non-polar (non humic) substances. Such decline was not observed in DMF extract alone by Schalekamp; his extract numbers appear to stabilize around 65 g/kg, a level just slightly above those noted in Figure II-2.7.

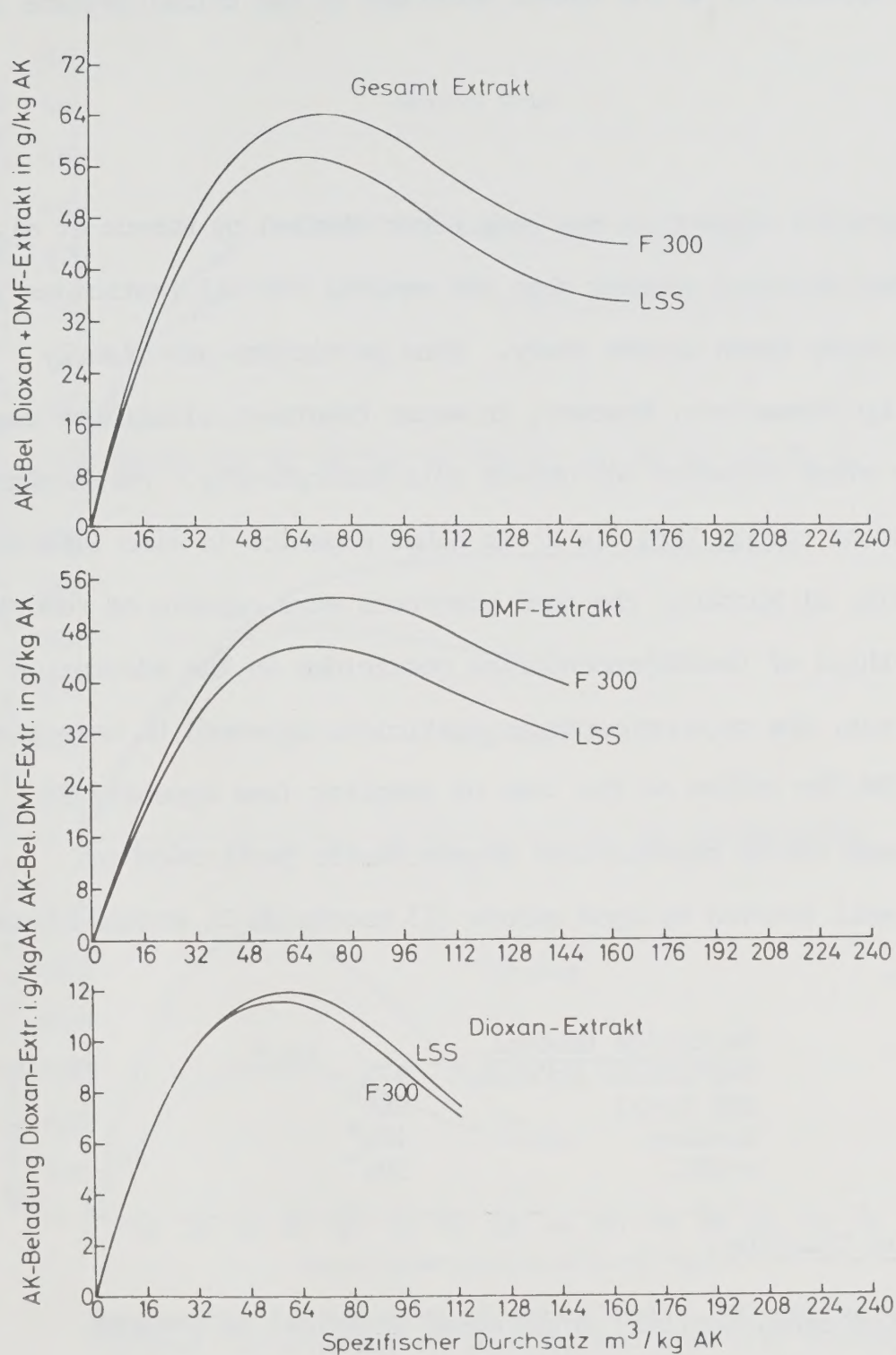
II-2.6 Chlorinated Organics

Trihalomethanes

The adsorption of trihalomethanes have been studied by Love et al. (1977), in laboratory powdered carbon as well as pilot column tests. The granular carbon tests indicated relatively rapid breakthrough, for chloroform, e.g., 17 days for a .75 m deep bed fed at 5 m/h at a feed concentration of 50 mg/l of chloroform. Doubling bed depth appeared to double carbon life, thereby, indicating a mechanism based on favourable adsorption. An approximate capacity of .5 g/kg of carbon was indicated and this appeared to be similar to the quantity predictable from isotherm calculations.

Under conditions similar to those indicated above, Mang (1977) obtained an approximate carbon life of only 3 weeks for trihalomethanes. Some adsorption is apparently retained in operating filters, however, for a long time beyond the early exhaustion point. At Morsang, for example, about 30% of the trihalomethanes were removed by carbon even after more than two years operation (see Appendix B).

FIGURE II-2.7. ORGANIC EXTRACTS FROM ACTIVATED CARBON AS A FUNCTION OF THROUGHPUT (FROM FUCHS AND KÜHN, 1977)



Waterworks filter with LS Supra and F 300 activated carbons. Dependence of loading on specific throughput

Gesamtextrakt: total extract

DMF: DMF

Beladung: loading

Spezifischer Durchsatz: specific throughput

In general, prevention of trihalomethane formation rather than adsorption appears to be the better solution to the trihalomethane problem.

Pesticides

Pesticide adsorption has been first studied by Robeck et al. (1965). They obtained greater than 99% removal for all pesticides in their laboratory fresh column study. Thus pesticides are clearly adsorbable by themselves, however, in water treatment situations competition by other organics may negate this adsorptivity. Furthermore, the question of carbon life vis a vis other organics is also important.

Again, at Morsang, the aged adsorbers were capable of removing almost two third of the organochlorine pesticides in the adsorption stage, whereas, the organophosphoric pesticides appeared to have been desorbed from the carbon at the time of sampling (see Appendix B).

Hansen (1977) reports that organochloric pesticides are relatively well removed by aged carbon (13 months to 21 months of use) as shown below:

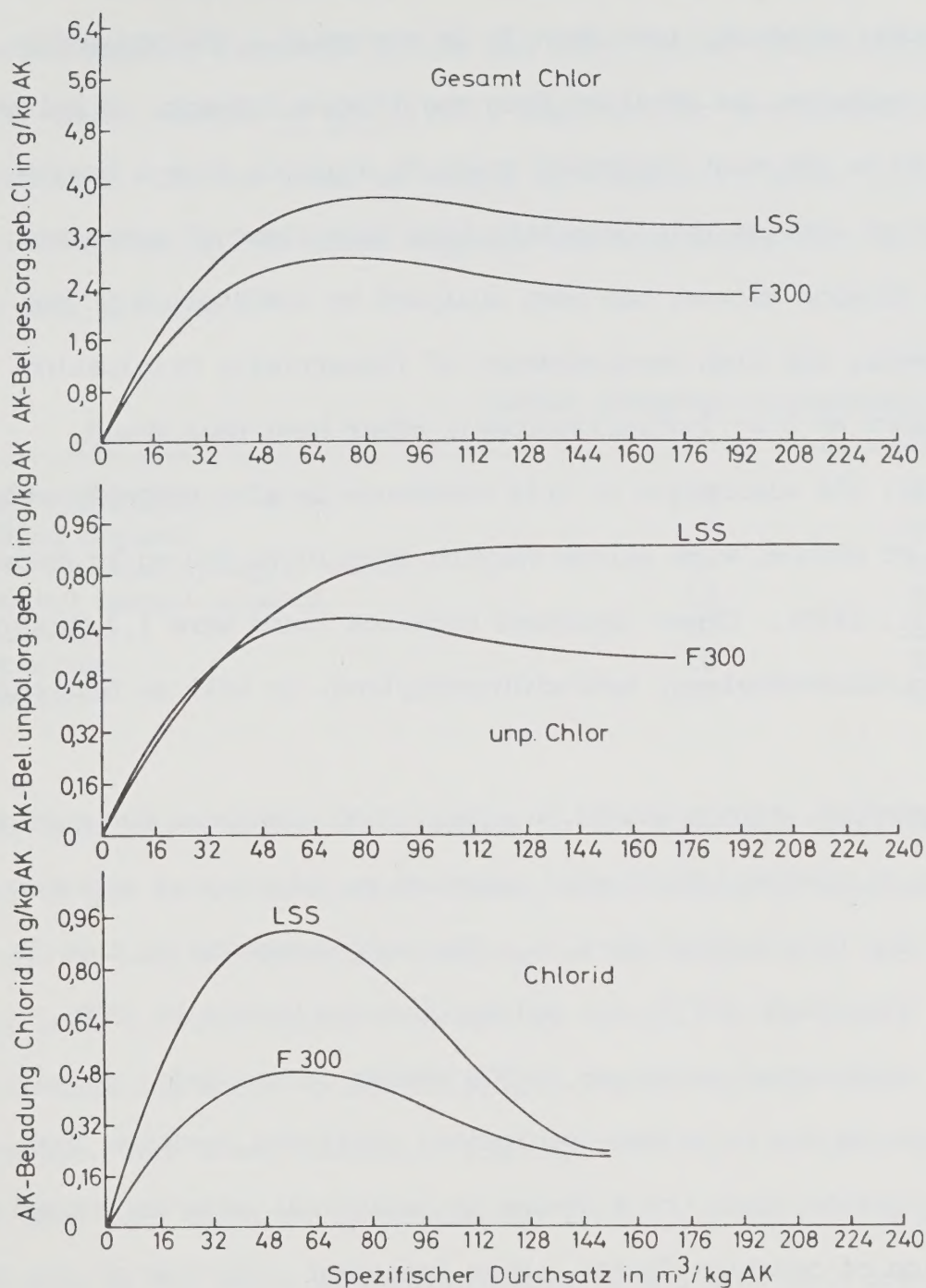
<u>Pesticide Removal</u>	
Heptachlor Epoxide	97%
BHC Total	86% ⁺
Lindane	40% ⁺
α -BHC	50% ⁺

Total Organic Chlorine

As indicated earlier, chlorinated organics, as a class, represent a most significant group of organics from a health effect standpoint. Investigators in West Germany applied a TOCl test (see Section I-1.3.2) to carbons from many water treatment plants.

As shown in Figure II-2.8, chlorinated organics are adsorbed similarly to DMF and Dioxane Extractable Organics with a maximum in

FIGURE II-2.8. CHLORINATED ORGANICS ADSORBED BY ACTIVATED CARBON AS A FUNCTION OF THROUGHPUT (FROM FUCHS AND KUHN, 1977)



Waterworks filter with LS Supra and F 300 activated carbons. Dependence of loading and specific throughput

Gesamtchlor: total chlorine

unp. Chlor: non-polar organic chlorine

Chlorid: chloride

Beladung: loading

Spezifischer Durchsatz: specific throughput

loadings obtained at about the same throughput. In the Düsseldorf filters, approximately 5% of the extractable organics can be identified as chlorinated, of which, less than 2% is non-polar. The non-polar chlorinated organics, as obtained from the dioxane extract, is believed in Germany to be the most important group of organics from a health effect point of view in this generally important class of compounds.

The dioxane extract has been analyzed by combination GC and micro-coulometry and high concentration of industrially originating substances such as bis-(2-chlorisopropyl) ether have been found. Interestingly, the adsorption of this substance is also strongly affected by the type of carbon, with values varying from 10 to 540 mg/kg carbon (Kölle et al., 1975). Other important organics found were 1,2 dichloropropanol, trichloroethylene, tetrachloroethylene, as well as hexachlorobutadiene.

In general, carbon should be a very good adsorbent for most two carbon atoms or greater chlorinated organics as chlorinated organics tend to be non-polar (see Section II-2.1). The only exception to this is reported by Schalekamp (1977) for polychlorinated biphenyls (PCB) who reports substantial increases in PCB across carbon beds. These increases, can be due to either desorption, continued reaction from the prechlorination stage, or a change in analytical accuracy caused by the adsorption of organics during carbon treatment. In view of the fact, that three separate analyses indicated the same trend and removal of interfering substances should decrease not increase concentrations, the second of the above explanations appears most likely.

II-2.7 Miscellaneous Organics

There are relatively few reports on the analysis of non-halogenated organic compounds before and after carbon adsorption. In an early study, Dostal et al. (1965), analyzed for the presence of industrial organics in the raw water as Nitro, W. Virginia. Table II-2.1 indicates that all of these organics are adsorbable with an approximately one week old bed.

	Carbon Adsorber Concentration in mg/l	
	In	Out
Bis(2-chloroethyl) ether	104	N.D.
2-Ethyl Hexanol	7	N.D.
Bis(2-chloroisopropyl) ether	23	N.D.
α -Methyl benzyl alcohol	12	N.D.
Acetophone	17	N.D.
Isophorone	16	N.D.
Tetralin	103	N.D.

Nine days later, a profile analysis in the same beds indicated, however, that to get to non-detectable levels (N.D.), beds as deep as 10 feet should be used at hydraulic loadings on the order of 13 m/h. As such deep beds or short carbon runs are not common, it is likely that the above organics start to breakthrough a column shortly after startup, although, with lower hydraulic loading, this may not occur quite as rapidly. PAH have been examined by Schalekamp (1977) who reported a general decrease on the order of approximately 50 and 100% with pre-ozonation but only 20% without pre-ozonation for the Zurich (Lengg) plant. In an earlier report (see Appendix B) PAH were reported essentially unchanged by treatment although the increase in PAH after prechlorination was apparently eliminated during treatment.

Research is continuing world wide on the diverse organics found in water and their removal by activated carbon bed through the use of the powerful mass spectrometry based analytical methods and, shortly, there will be very much more data in the literature. Nonetheless, these data will be of limited use unless proper interpretation techniques are used and the carbon conditions are carefully given.

II-2.8 SUMMARY

Pretreatment prior to carbon is important in removing suspended, colloidal, and some macromolecular organics. In general, ozonation tends to decrease adsorptivity but increase biodegradation rates. Carbon columns are generally considered to sustain an active biologically fauna that oxidize substantial quantities of organics. Bacterial growth, however, in a water treatment adsorber can result in high effluent bacterial counts unless frequent backwash and post-disinfection are practiced.

Lumped organic parameters (e.g., TOC) indicate that initially as much as 90% of feed organics are removed by adsorption, however, this removal exponentially declines to some constant value essentially attributable to biodegradation. Taste and odour compounds, however, may continue to be removed by adsorption well beyond the biodegradation removal stage.

Trihalomethanes breakthrough somewhat ahead of lumped organics, typically, at bed depths below 1 m, a bed life of only one month can be expected. In contrast, other chlorinated organics, e.g., organochlorine pesticides, are adsorbed relatively well by carbon over periods beyond the declining region of lumped organic adsorption.

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III-1.1 Introduction

Studies were conducted at McMaster University to determine the treatability by activated carbon of Canadian drinking water supplies and to aid in the interpretation of the previously reviewed European data to Canadian conditions. The characteristics of water supplies, equilibrium adsorption, adsorption kinetics and long term column performance, and in addition, the best choice of carbons were determined. Furthermore, the computer prediction technique of Peel and Benedek (1975) was adopted to water treatment and the results were interpreted with the aid of this model.

III-1.2 Experimental

Equilibrium carbon adsorption isotherms were conducted according to Benedek (1974) with slight modifications. Sample volumes were increased to 250 ml. Orbital shakers used were modified to take sixteen 500 ml glass stoppered Erlenmeyer flasks. Samples were filtered before analysis.

Five activated carbons were considered for this study and were evaluated with the lake water supply. The five are: PX-21 and PX-24M, petroleum base, from Amoco Research Corp., Filtrasorb-400, bituminous coal base, from Calgon Corp., Darco S51, lignite base, from ICI America, and Witco 512, petroleum base, from Witco Inc. The properties of these three carbons are given in Tables II-1.1 and II-1.2

Adsorption kinetics were run in the same apparatus as the isotherms. Flasks were removed at different times and immediately filtered to remove the carbon. Each flask contained 120 mg F-400 in 250 ml water.

Cellulose nitrate membrane filters with 0.2 μ pore size were used exclusively for all filtration. The filters were soaked in distilled water at least over night and rinsed until no further TOC was washed from the filter, 200 ml distilled water is usually sufficient.

Distilled water was prepared by distilling predistilled water from permanganate solution according to Smith (1972).

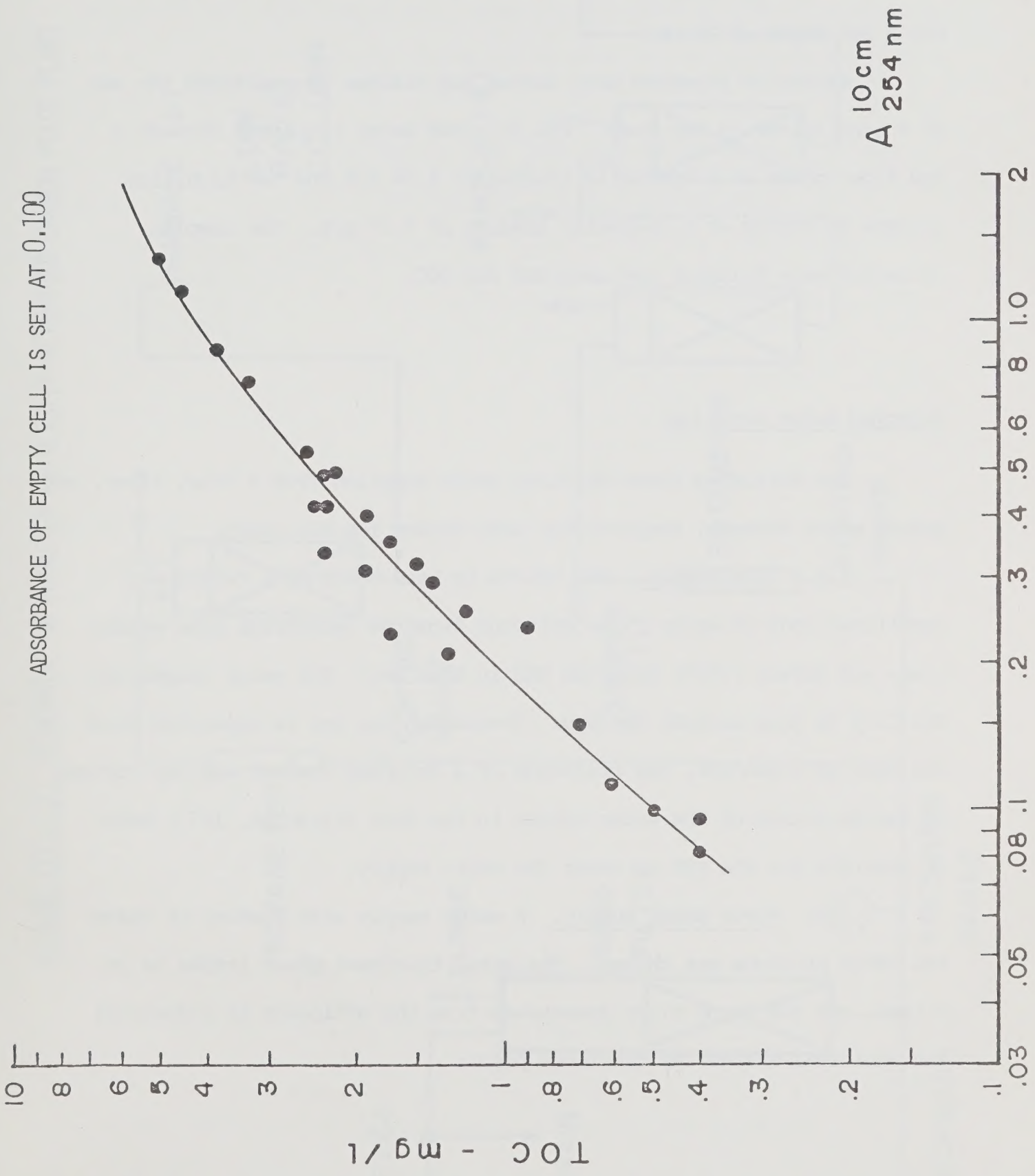
TOC analysis was conducted with a Bausch and Lomb Spectronic 21-UV-D spectrophotometer using 10 cm cell at 254 nm. The UV-TOC analysis follows Dobbs (1972) work. The close examination of Dobbs' system indicated that sensitivity could be increased with a longer than 5 cm cell. Therefore a 10 cm cell was used in the present system. The Spectronic 21-UV-D was calibrated with the TOC analysis system of the Canada Centre for Inland Waters (Goulden, 1976). The absorbance of the empty optical cell was set at 0.100, as reliable zero base line calibration was not available. The calibration curve is shown in Figure III-1.1

The total organic chloride was measured by a system developed along the lines of the system described by Kuhn and Sontheimer (1973) (described in detail in Appendix C).

The analysis for polynuclear aromatic hydrocarbons (PAH) followed Borneff (1969), on Merck alumina, 0.25 mm x 20 cm x 20 cm TLC plates. Detailed description is placed in Appendix C.

FIGURE III-1.1. TOC CALIBRATION

ADSORBANCE OF EMPTY CELL IS SET AT 0.100



Logistic considerations necessitated the use of the finished lake water for the carbon pilot plant study. Figure III-1.2 is the schematic of the pilot plant set up. The columns are 5 cm id PVC tubes with flow distributed entrances and exits. Each column contains 162.3 gm F-400 for a bed depth of 20 cm.

Excessive pressure drop across the columns necessitated the use of a sand filter in the feed. The filtered water is passed through a low flow column at a hydraulic loading of 1.24 m/h and two high flow columns in series at a hydraulic loading of 7.37 m/h. The samples collected were filtered and analyzed for TOC.

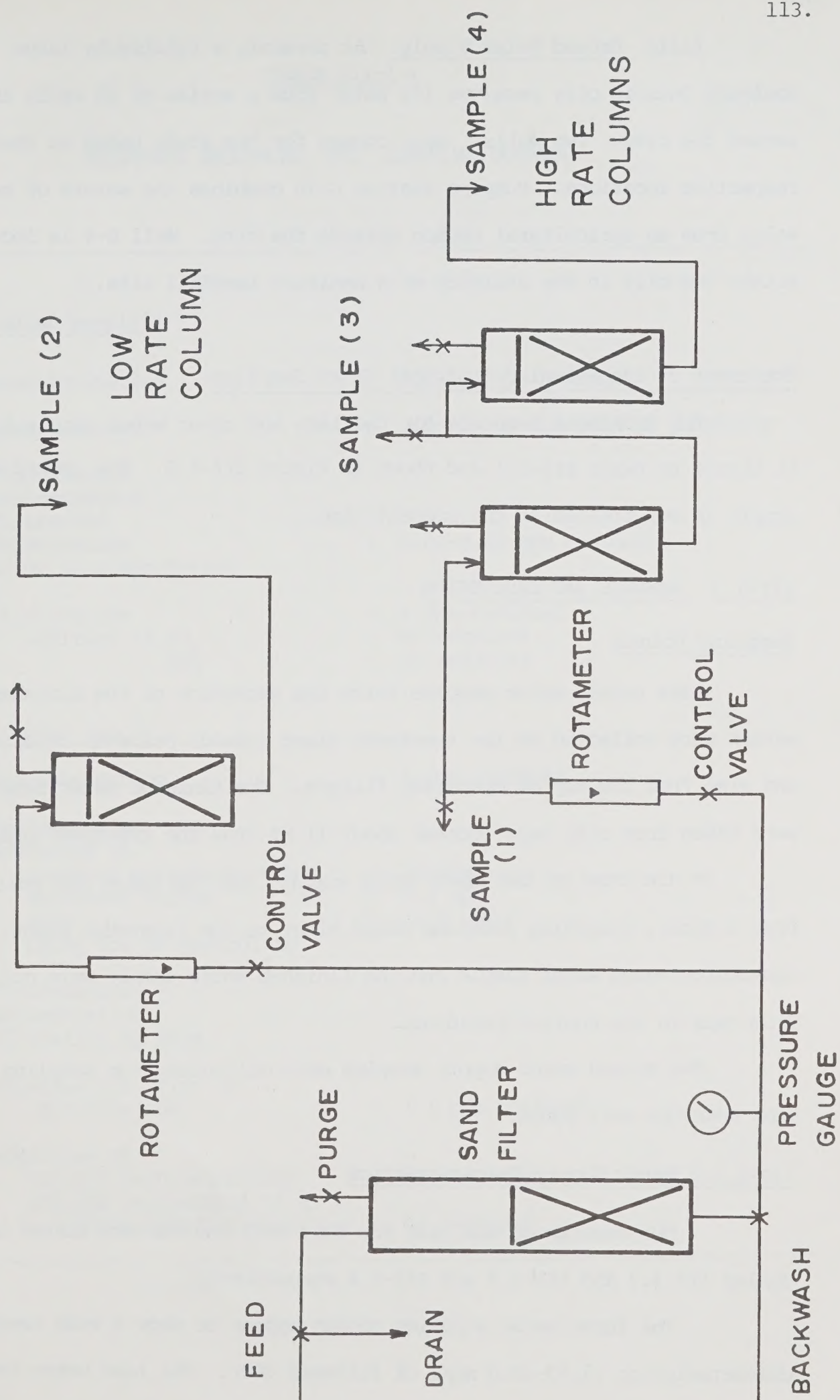
Selected Water Supplies

The following three drinking water supplies from a lake, river, and ground water sources, respectively were chosen for the study:

(i) Lake Supply. The source is Lake Ontario, a relatively unpolluted body of water. The effluent from the industrial area enters a Bay and Meresz (1977) detected PAH in this Bay. The water intake for the City is just outside the Bay. Eventhough the Bay is separated from the Lake by a sandbar, the existence of a shipping channel and the current in the direction of the water intake in the lake (Strachan, 1977) make it possible for the PAH to enter the water supply.

(ii) River Water Supply. A water supply with history of taste and odour problems was chosen. The water treatment plant intake is in a canal off the Grand River downstream from the effluents of industrial and municipal wastewater treatment plants.

FIGURE III-1.2. SCHEMATIC OF McMASTER UNIVERSITY ACTIVATED CARBON PILOT PLANT



(iii) Ground Water Supply. At present, a relatively large Southern Ontario city receives its water from a series of 80 wells in and around the city. Two wells were chosen for the study based on their respective locations. Pumping station G-20 combines the waters of several wells from an agricultural region outside the city. Well G-4 is located within the city in the vicinity of a sanitary landfill site.

Treatment of the Selected Municipal Water Supplies

The treatment sequence for the lake and river water supply systems is listed in Table III-1.1 and shown in Figure III-1.3. The ground water supply is not treated at the present time.

III-1.3 RESULTS AND DISCUSSION

Sampling Points

Lake supply water samples (with the exception of the finished water) were collected on the treatment plant grounds prior to chlorination and also from the top of operating filters. The finished water samples were taken from city taps located about 11 km from the treatment plant.

In the case of the river water supply, the raw water was collected from a canal, branching from the Grand River to the treatment plant. The superchlorinated water sample and the finished water sample were collected from taps in the control building.

The ground water supply samples were collected from sampling taps near the well pumps.

III-1.3.1 Water Supply Characteristics

The results of analysis for TOC, TOCl and PAH are listed in Tables III-1.2 and III-1.3 and III-1.4 respectively.

The three water supplies chosen appear to show a wide range in characteristics (1.03-10.0 mg/l of filtered TOC). The lake water is

TABLE III-1.1

TREATMENT SEQUENCES AND CHEMICAL DOSAGES.

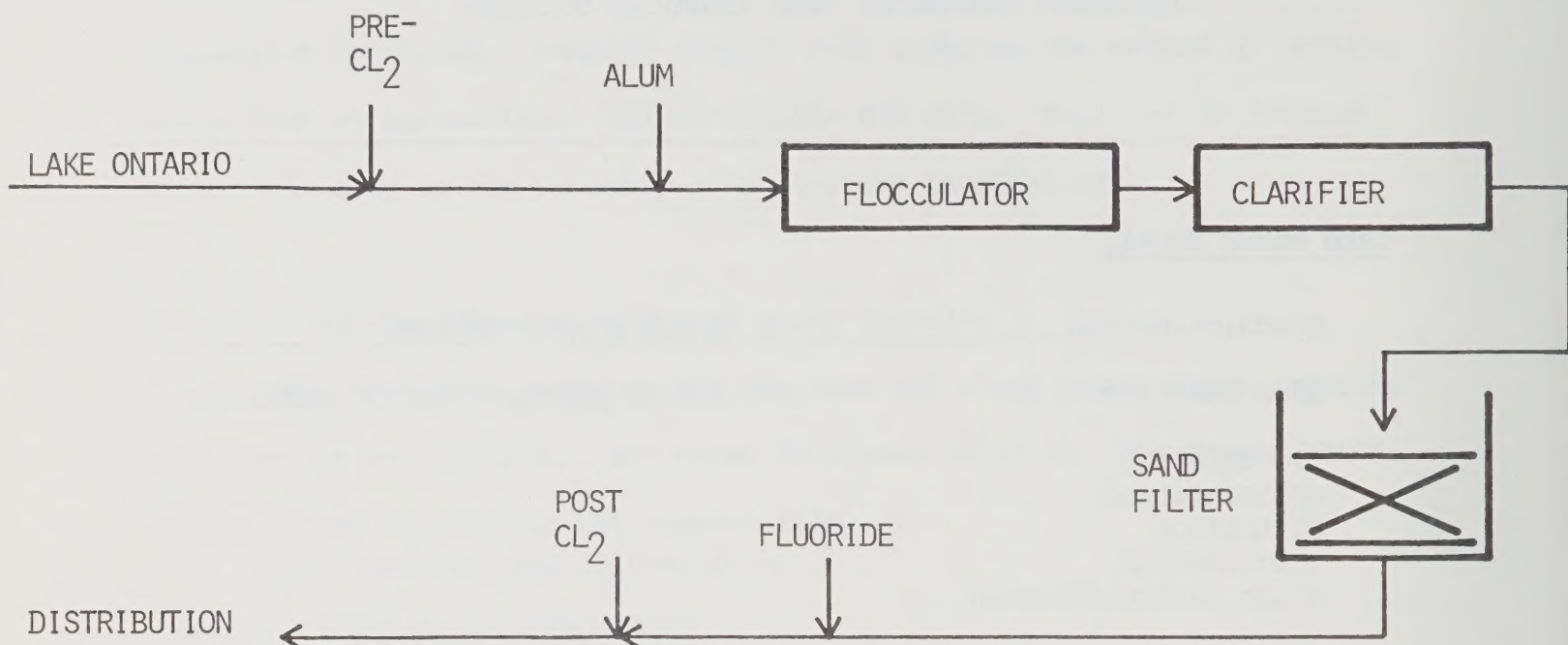
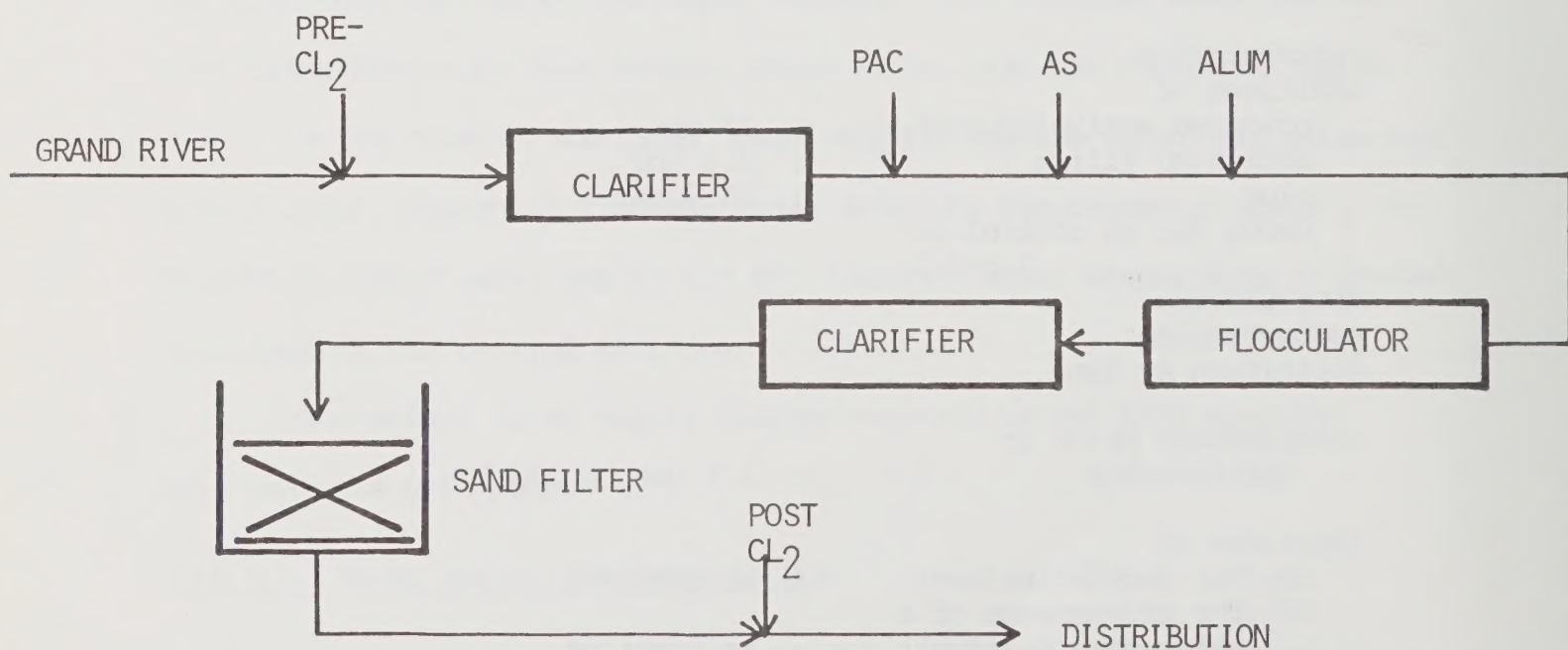
Lake water supply

prechlorination	: 1.0-1.2 ppm residual
alum addition	: 7.5-20 ppm function of turbidity
flocculation	
sedimentation	
filtration	
chlorination	: 0.60-0.65 ppm residual
prior to distribution	
fluoridation	: 1 ppm residual
addition of SO ₂	: as required
NH ₃	: as required

River water supply

prechlorination	: 5 ppm residual
sedimentation	
additions of	
powdered activated carbon	: 15 ppm
activated silica	: 3.4 ppm
alum	: 10.7 ppm
CaCO ₃ for pH control to 7.5-7.7	
flocculation	
sedimentation	
filtration by sand	
chlorination prior to distribution	: 1.1 ppm residual
additions of	
SO ₂ (for dechlorination)	: as required
NH ₃ (for maintenance of a chloramine residual)	: as required

FIGURE III-1.3. TREATMENT SCHEMATICS FOR LAKE AND RIVER WATER SUPPLIES

LAKE WATER SUPPLYRIVER WATER SUPPLY

PAC: POWDERED ACTIVATED CARBON
AS: ACTIVATED SILICA

TABLE III-1.2. SUMMARY OF TOC DATA

WATER	COLLECTION DATE	TOC - mg/l	
		Filtered	Unfiltered
Lake: Raw " "	77.6.8	2.05	2.45
	77.9.29	2.20	2.20
Lake: Prefilter " "	77.6.8	1.75	2.20
	77.9.29	1.55	1.70
Lake: Tap " " " " " " " "	77.6.2	1.50	1.90
	77.6.3	1.55	2.15
	77.6.30	1.47	1.70
	77.10.8	1.43	1.91
	77.11.1	1.42	1.70
River: Raw " "	77.6.15	4.75	5.5
	77.9.30	10.0	-----
River: Pre Cl ₂ " "	77.6.15	3.65	4.65
	77.9.30	5.70	-----
River: Tap " "	77.6.15	3.70	4.15
	77.9.30	5.50	5.65
Ground: G-4 " "	77.6.21	2.70	3.90
	77.11.1	2.52	3.50
Ground: G-20 " "	77.6.21	1.03	1.10
	77.11.1	1.05	1.10

TABLE III-1.3. SUMMARY OF TOCl DATA

WATER	RAW TOC mg/l	AC DOSE gm/l	POST AC TOC mg/l	ORGANIC Cl ⁻ -mg/l		
				RUNS		
				1	2	3
Lake: Raw	2.20	.4090	.67	.16	.60	---
Lake: Prefilter	1.55	.3066	.61	.27	.45	.90
Lake: Tap	1.43	.2576	.64	.87	.22	.11
Lake: Tap	1.42	1.5030	.405	.64	.33	---
River: Raw	10.0	1.5045	1.45	.58	.27	.68
River: Post Cl ₂	5.7	1.0934	1.78	1.16	.66	1.00
River: Tap	5.5	1.6737	1.06	1.07	.97	.74
River: Tap	5.5	.6326	2.4	.34	.52	.58
Ground: G-20	1.05	1.5056	.47	1.16	.28	---
Ground: G-4	2.52	1.5046	.42	.27	.28	---

TABLE III-1.4. SUMMARY OF PAH DATA

WATER	AC DOSE gm/l	PAH - $\mu\text{g/l}$ as Fluoranthane		
		Total	Fluoranthane	Other
Lake: Raw	nil	0.44	0.29	0.15
	.4090	1.18	0.48	0.71
Lake: Prefilter	nil	0.84	0.38	0.46
	.3066	0.29	0.20	0.09
Lake: Tap	nil	3.03	2.98	0.05
	.2576	1.22	0.56	0.66
River: Raw	nil	0.05	0.03	0.02
	1.5045	0.67	0.26	0.41
River: Pre Cl ₂	nil	0.27	0.06	0.21
	1.0934	0.60	0.30	0.30
River: Tap	*	0.57	0.25	0.32
	1.6737 *	0.65	0.25	0.40
Ground: G-20 G-4	nil	0.44	0.22	0.22
	nil	0.40	0.24	0.16
* 15 mg/l powdered activated carbon is used in the treatment process				

similar to the river Seine in France. Among the ground water sample G20 appears to be of excellent quality while G-4 may be contaminated by leachates as its TOC level is well above that of G-20 and most importantly a relatively high level of suspended or near colloidal, UV absorbing, materials appear to be present in G-4.

The TOC level of the treated lake supply appears to be somewhat above those of similar European water supplies. In particular sand filtration appears to remove very little of the organics. Nonetheless the treated water, just as the raw water, is quite low in organics. On the other hand the river water organic level appears to be several times above the levels obtained in Europe on similar raw water supplies. This indicates that the water may receive inadequate treatment at this particular site and as this site has acceptable treatment by Canadian standards, the present Canadian treatment practices may prove inadequate in the long run.

The variation is minimum for the lake supply and appears to be highest for the river supply. This indicates the great potential danger of contamination of a river supply from spills of organic materials. The filtered TOC of the treated river water is also very high, well above the levels obtained in France from the Seine.

The TOC1 data in Table III-1.3 shows considerable inconsistencies due to possible interferences as discussed in Appendix C. At the time of this writing, not all of the problems have been worked out. Nevertheless, some trends may be discussed such as the increases in TOC1 concentration if the water is chlorinated. This trend was expected in accordance with many EPA publications. Fuchs and Kuhn (1976) obtained TOC1 levels of 0.4-0.6 mg/l for a Rhein river water supply.

The measurement of PAH are also full of pitfalls. The PAH levels listed in Table III-1.4 bear this out. Apparently, the levels, in both lake and river water supplies increase with treatment and the PAH levels increase after carbon treatment. However both phenomenon are possibly connected with (on the basis of visual observations and difficulties with TLC plate developments) the presence of organics, most likely humic substances, that mask or adsorb the PAH.

The direct extraction procedure can be credited with indiscriminately introducing the interferring organics. To eliminate most of the interferring organics, Saxena (1977) uses polyurethane foam to selectively adsorb the PAH. Then the PAH are eluted from the foam with cyclohexane. Apparently the system is quite successful. This modification has been revealed too late to be applied in this study. Both conventional and carbon treatment remove organics, may remove interferences and allow more representative levels. Thus the PAH levels in Table III-1.4 can be considered as minimum with real levels probably above those obtained after carbon treatment.

The "other PAH" listed in Table III-1.4 appeared separated from fluoranthene, a four ring PAH, and travelled a shorter distance along the TLC plates. The comparison of spot positions of the calibration standards and of the unknown samples indicate that these "other PAH" spots constitute the next heavier group of PAH's, the five ring compounds. This group possibly includes benzo(a) pyrene, benzo(e) pyrene and benzo(b) fluoranthene, all relatively active carcinogens, benzo(a) pyrene being the most active (Harrison et al., 1975).

III-1.3.2 Adsorptivity of Selected Water Supplies

Carbon Choice Based on Isotherms

Adsorption isotherms depict the equilibrium loading of organics on the carbon on a per unit weight basis. The organics may be measured as individual compounds where possible or, in a complicated mixture such as water, in terms of TOC.

Figures III-1.4 and III-1.5 compare isotherms of five different carbons. The criteria for selecting carbons are:

(i) carbon capacity, q , at any given equilibrium solution concentration, and

(ii) residual concentration at large carbon dosage.

On the basis of the above criteria, PX-24M and Witco 512 are clearly worse than the other three carbons and, further adsorptivity work, has been restricted to these three carbons. Among the three carbons, Filtrasorb 400 and PX-21 show best performance; PX-21 due to its high surface area has the greatest capacity, however, Filtrasorb 400, is capable of absorbing a greater fraction of the organics present. Since F400 has a lower price and better commercial backup, work on adsorption kinetics and column work has been restricted to F400.

Isotherms of Selected Water Supplies

Isotherms on the Lake water supply are shown in Figures III-1.4 to III-1.6. There is almost no difference among the three plots as the water quality, indicated by filtered TOC, changes very little between the Lake and the finished water source. The TOC was 2.0 mg/l in the raw water and 1.5 in the tap water. Non-adsorbable residuals of about .4 mg

FIGURE III-1.4. ADSORPTION ISOTHERMS WITH LAKE RAW WATER

INITIAL TOC CONCENTRATION = 2.05 mg/l

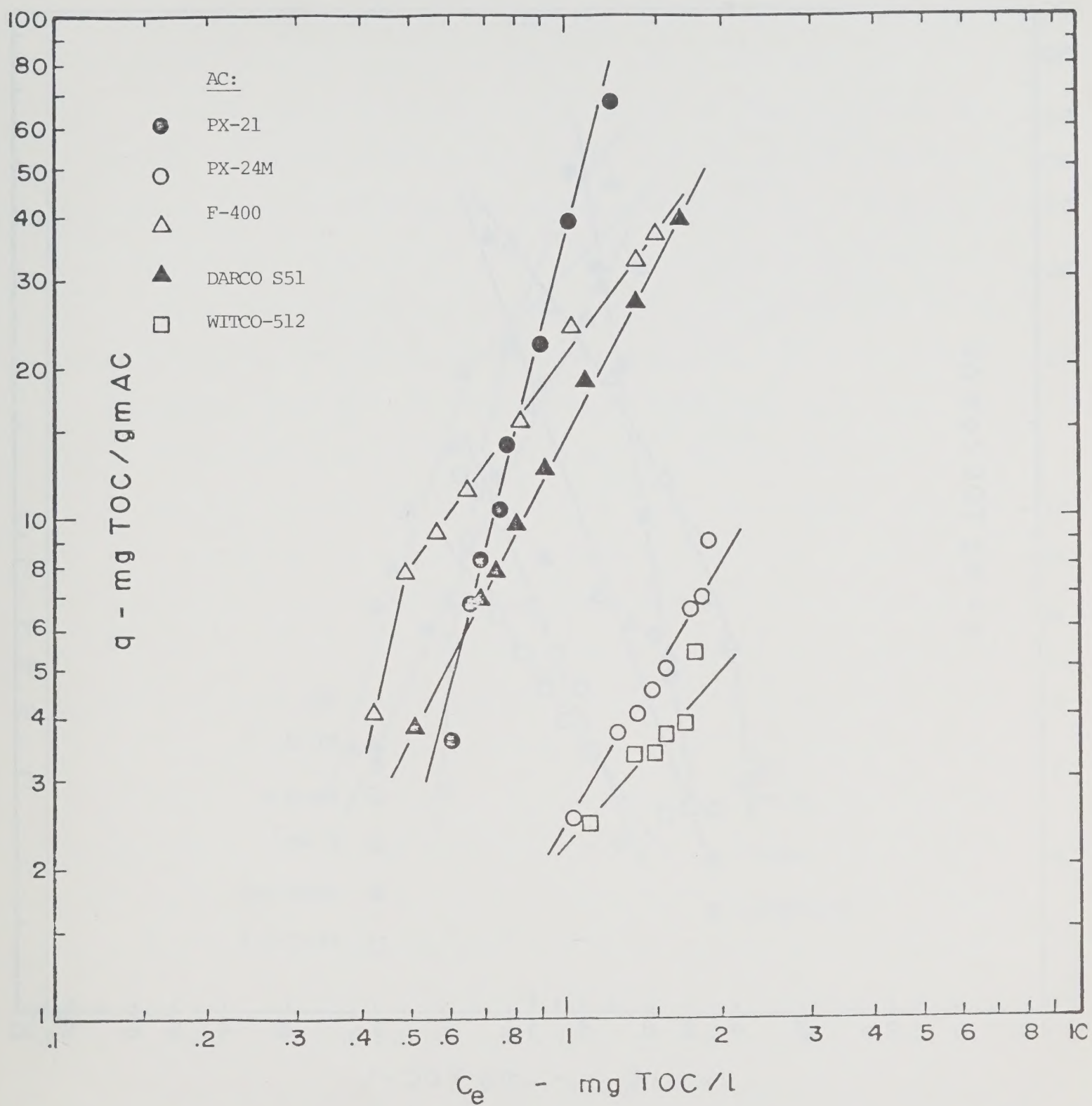


FIGURE III-1.5. ADSORPTION ISOTHERMS WITH LAKE TAP WATER

INITIAL TOC CONCENTRATION = 1.5 mg/l

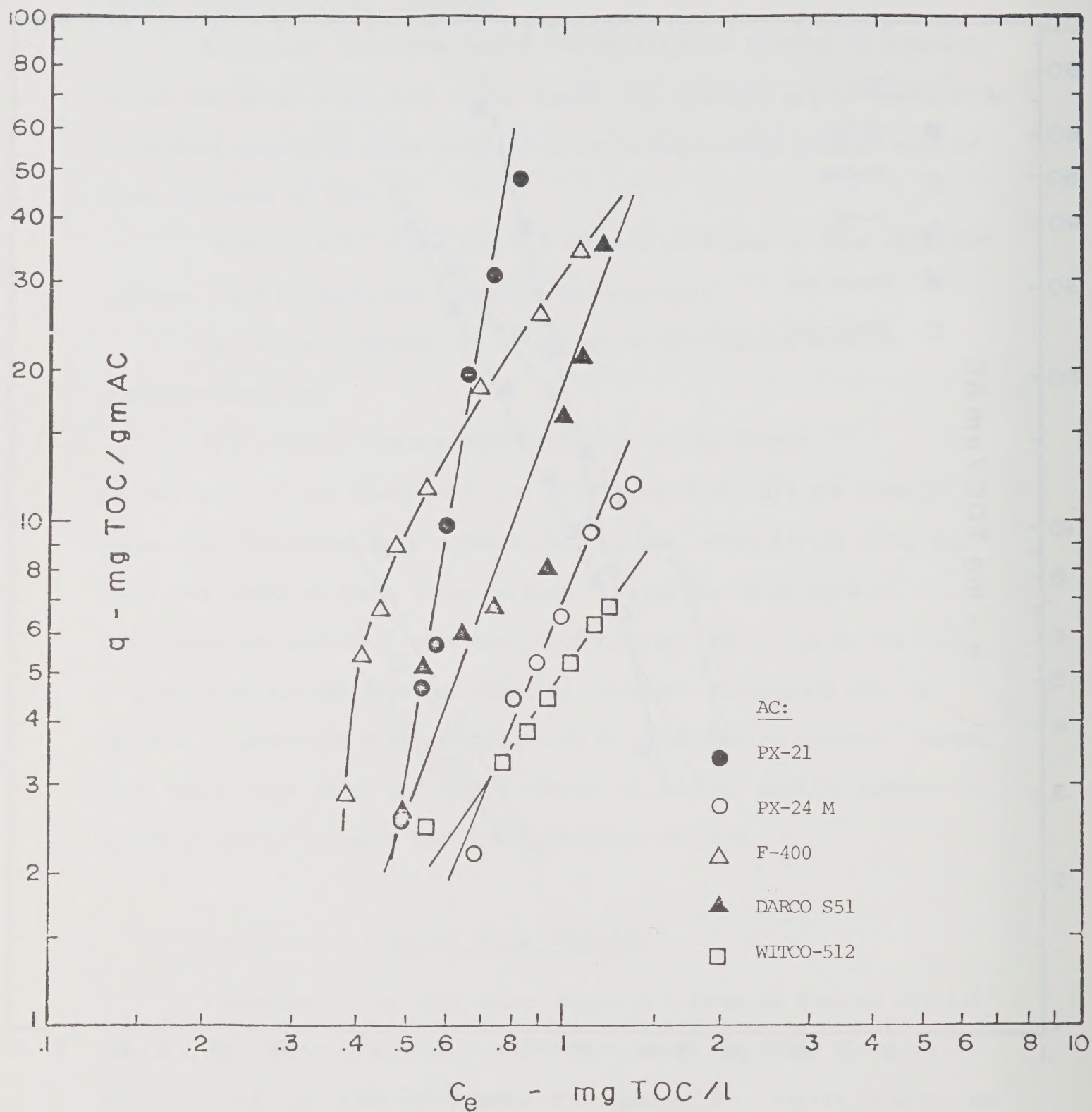
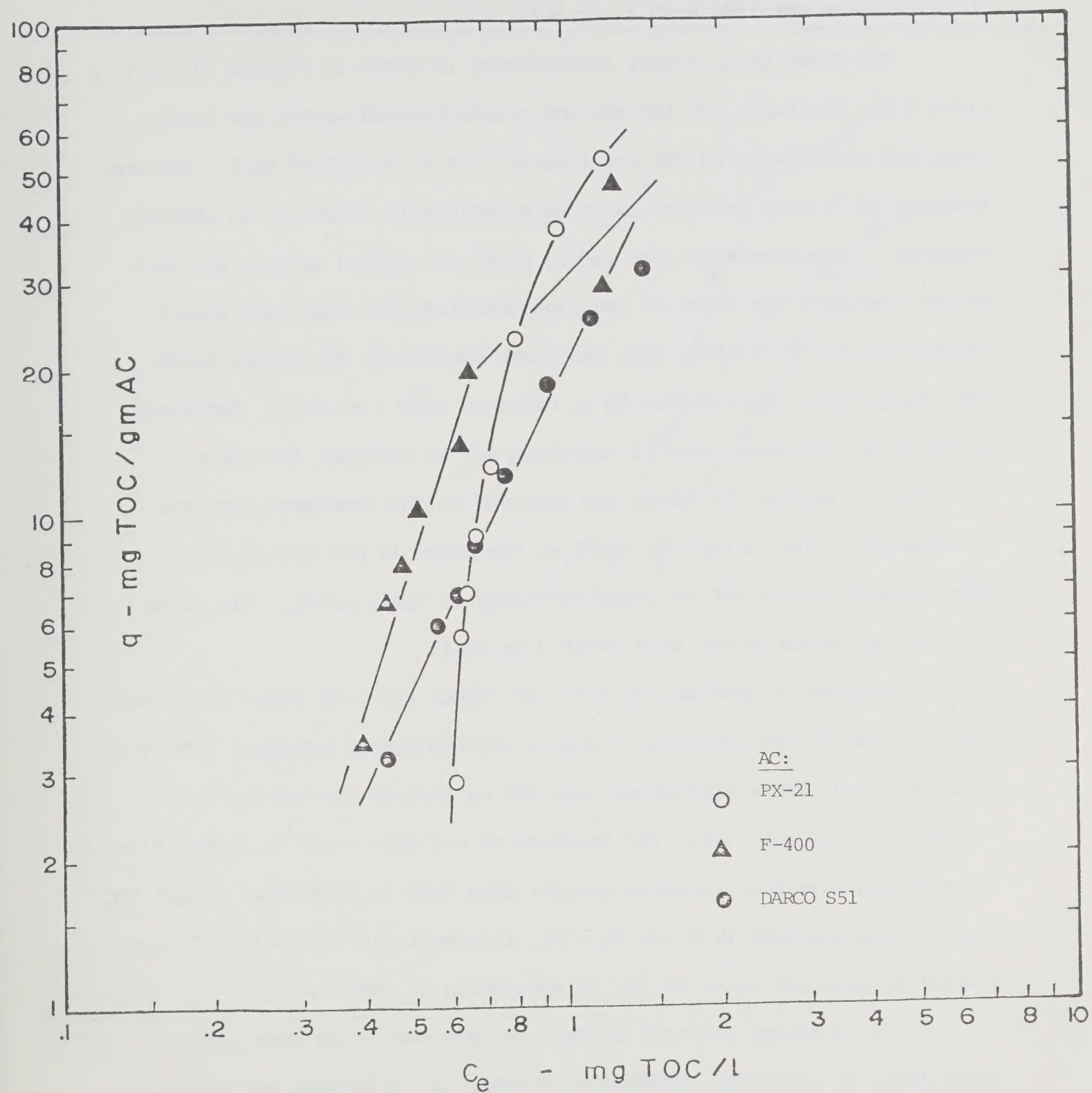


FIGURE III-1.6. ADSORPTION ISOTHERMS WITH LAKE PRE-FILTER WATER

INITIAL TOC CONCENTRATION = 1.75 mg/l



TOC/l were obtained with 400 mg AC/l and maximum loadings of 50-80 mg TOC/gm AC were obtained with 10 mg AC/l.

The River water supply adsorptivity is shown in Figures III-1.7 to III-1.9. The isotherms for the raw and prechlorinated waters are nearly identical even though the TOC was reduced from 4.75 to 3.65 mg/l. Maximum loadings of 7% were obtained along with negligible reduction in residual organics. Non-adsorbable TOC levels were not reached as only 400 mg/l AC was used, and the shape of the isotherms indicate that such levels (assume 0.4 mg TOC/l as in Lake isotherms even though the levels could vary among water supplies) could be obtained with 3 gm AC/l. Isotherms of the River tap water show a reduction in the residual TOC while no reduction in initial TOC level was achieved in the treatment past pre-chlorination. The 15 mg/l AC added at the plant is not enough to substantially affect TOC as these isotherms so aptly prove. The .4 mg/l TOC residual could be met with about 2 gm AC/l.

Isotherm of groundwater G-20 in Figure III-1.10 shows very steep lines indicating the presence of mostly non-adsorbable organics. The 0.4 mg/l TOC level can be approached with 100 mg AC/l as the initial TOC concentration is also low. The isotherm of G-4 well water in Figure III-1.11 shows a wider range of organics present than that in G-20. The .4 mg/l TOC residual was achieved with 400 mg AC/l. Interestingly this water is very similar to Lake tap water as far as adsorption is concerned.

The isotherms prepared through the McMaster study show strong resemblance to isotherms prepared in Europe, i.e. at Morsang sur Seine, France (see Benedek, 1977).

FIGURE III-1.7. ADSORPTION ISOTHERMS WITH RIVER RAW WATER

INITIAL TOC CONCENTRATION = 4.75 mg/l

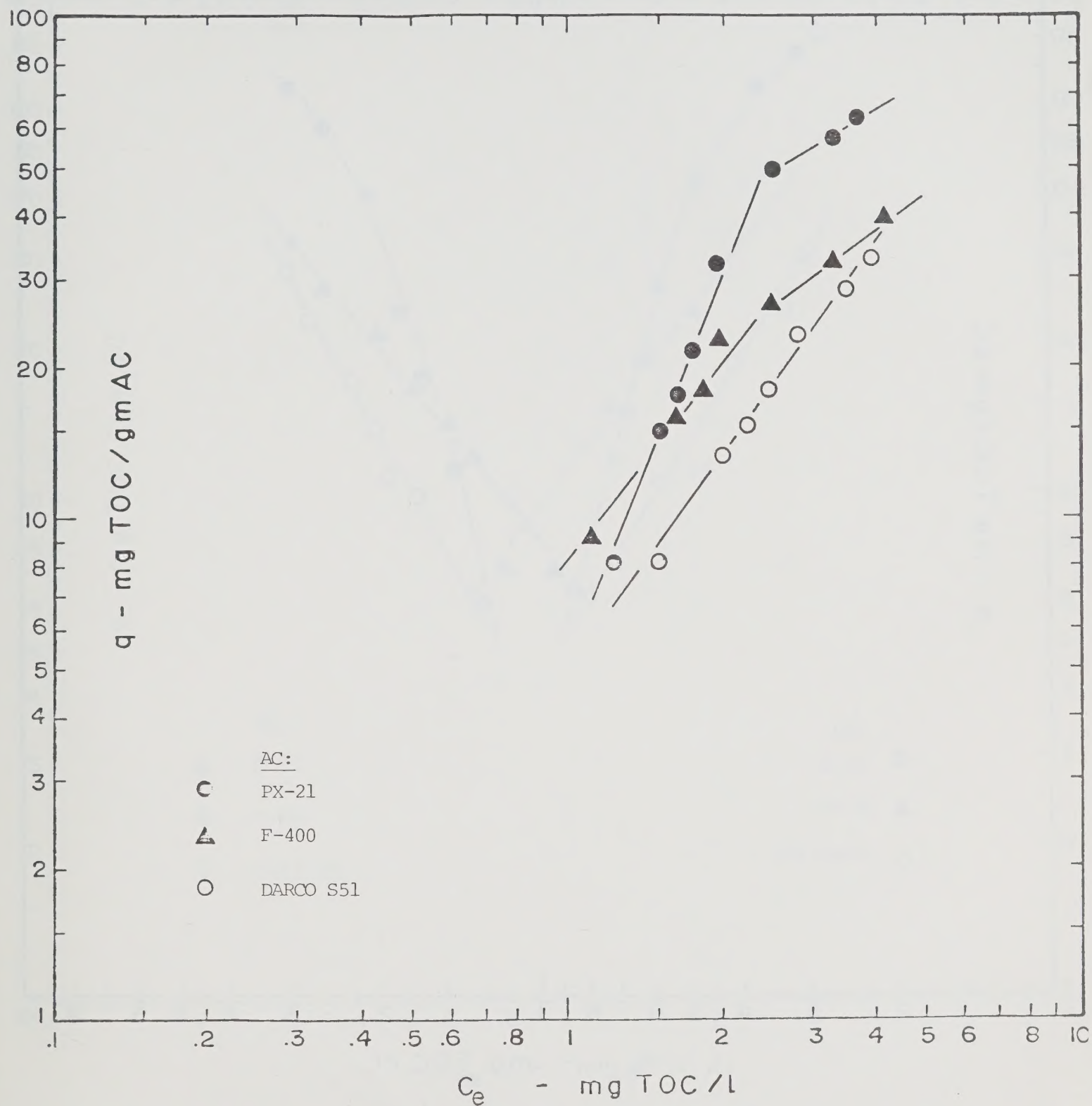


FIGURE III-1.8. ADSORPTION ISOTHERM WITH RIVER PRECHLORINATED WATER

INITIAL TOC CONCENTRATION = 3.65 mg/l

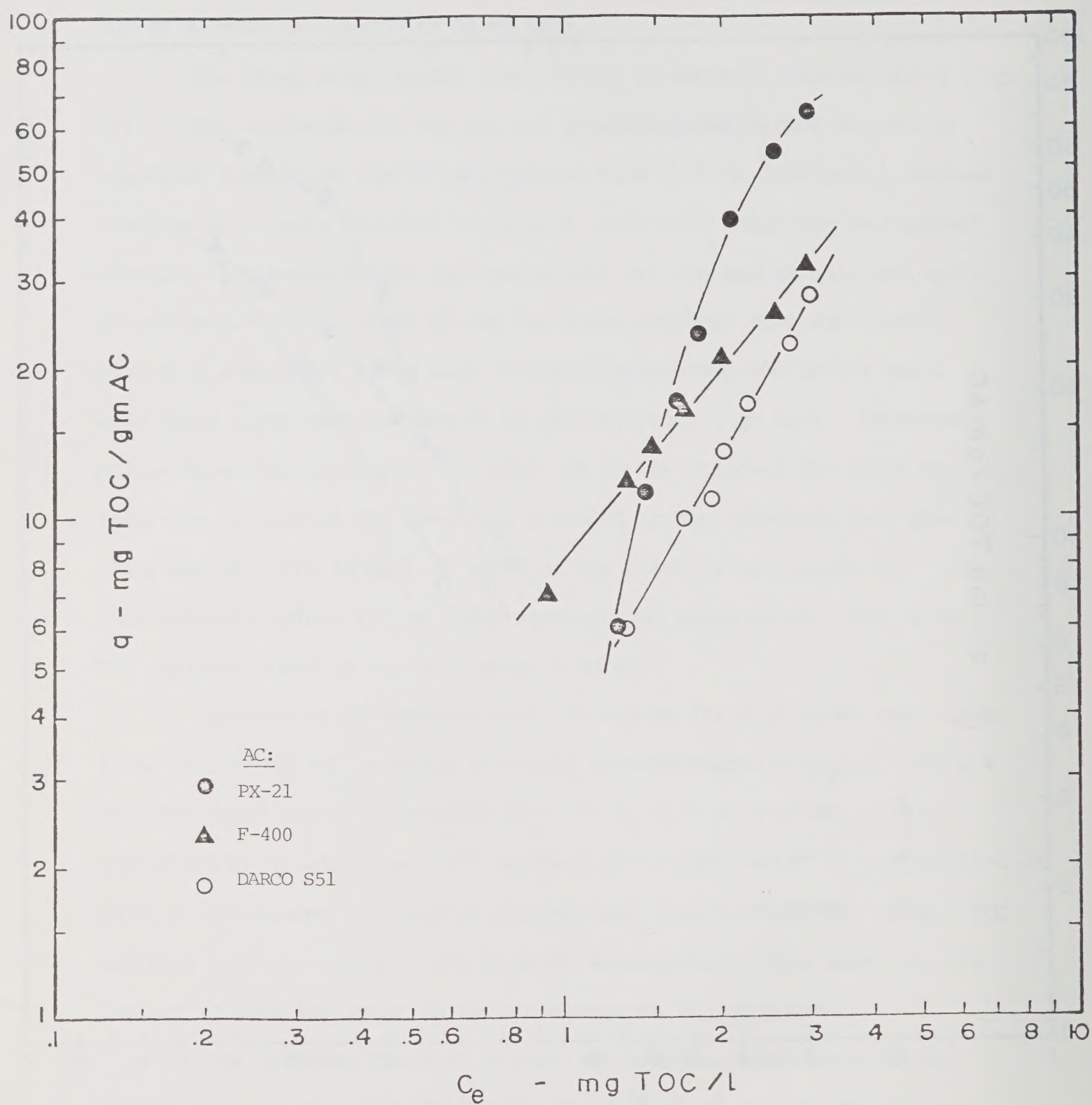


FIGURE III-1.9. ADSORPTION ISOTHERMS WITH RIVER TAP WATER

INITIAL TOC CONCENTRATION = 3.7 mg/l

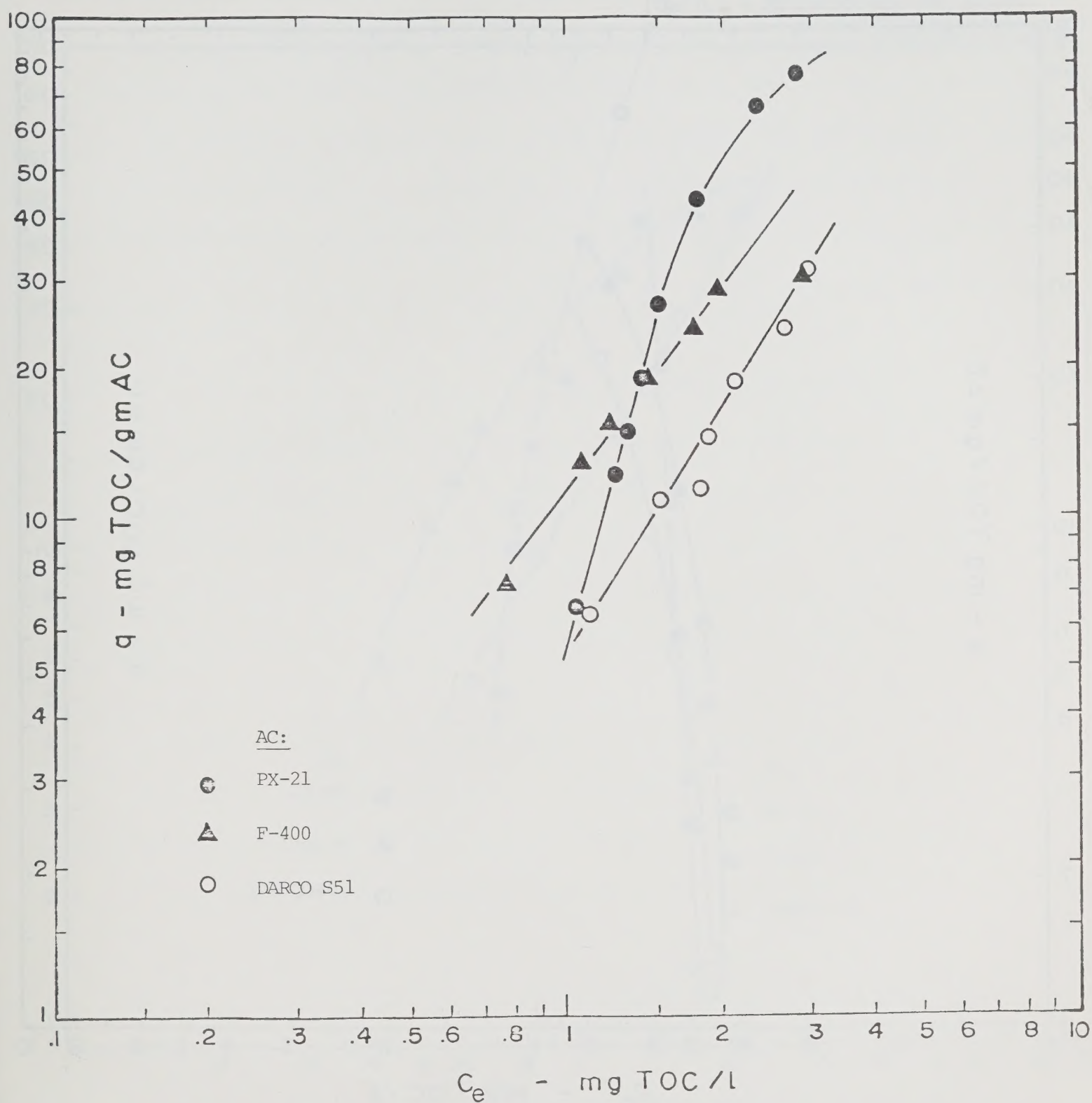


FIGURE III-1.10, ADSORPTION ISOTHERMS WITH GROUND G-20 WELL WATER

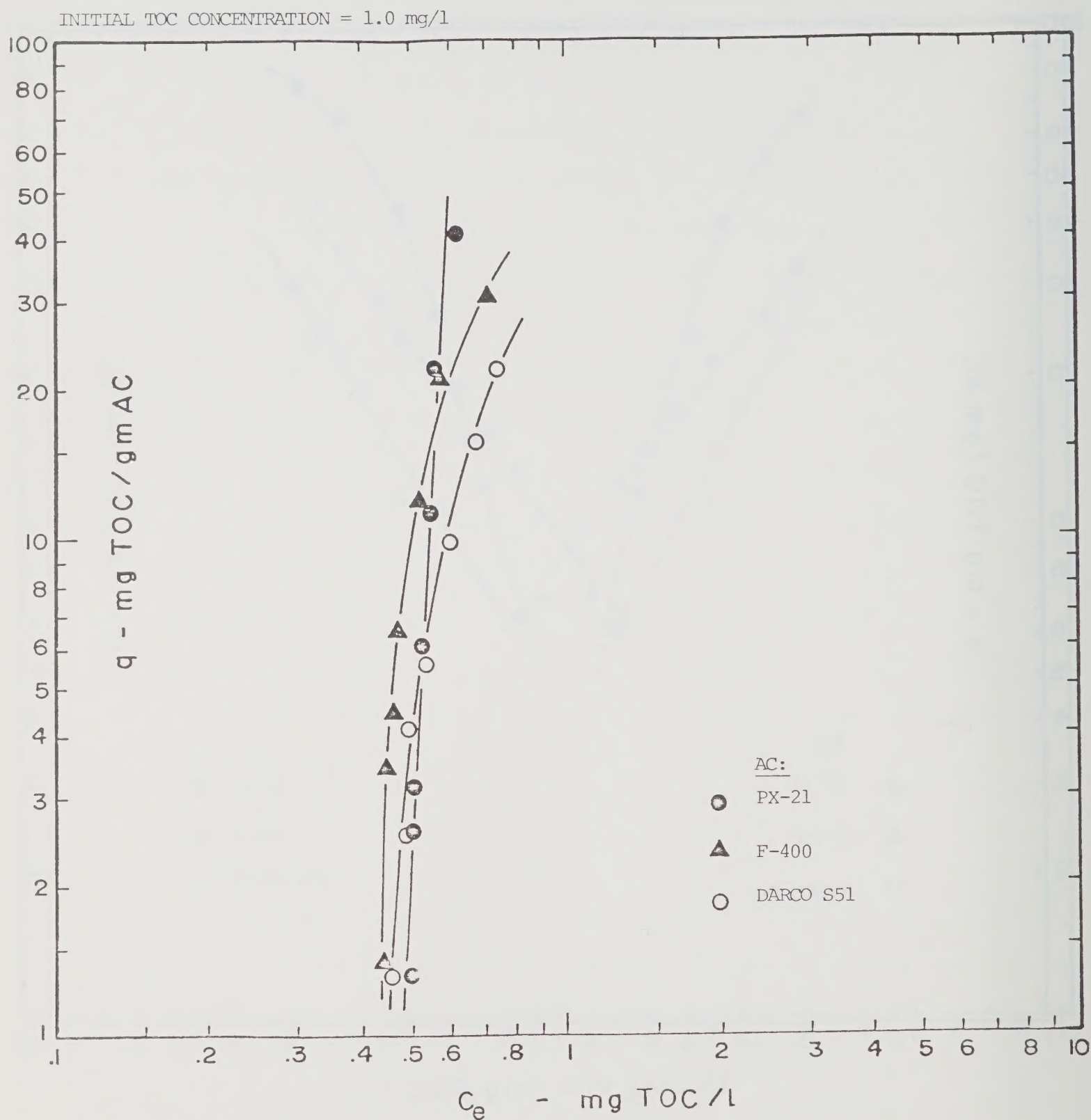
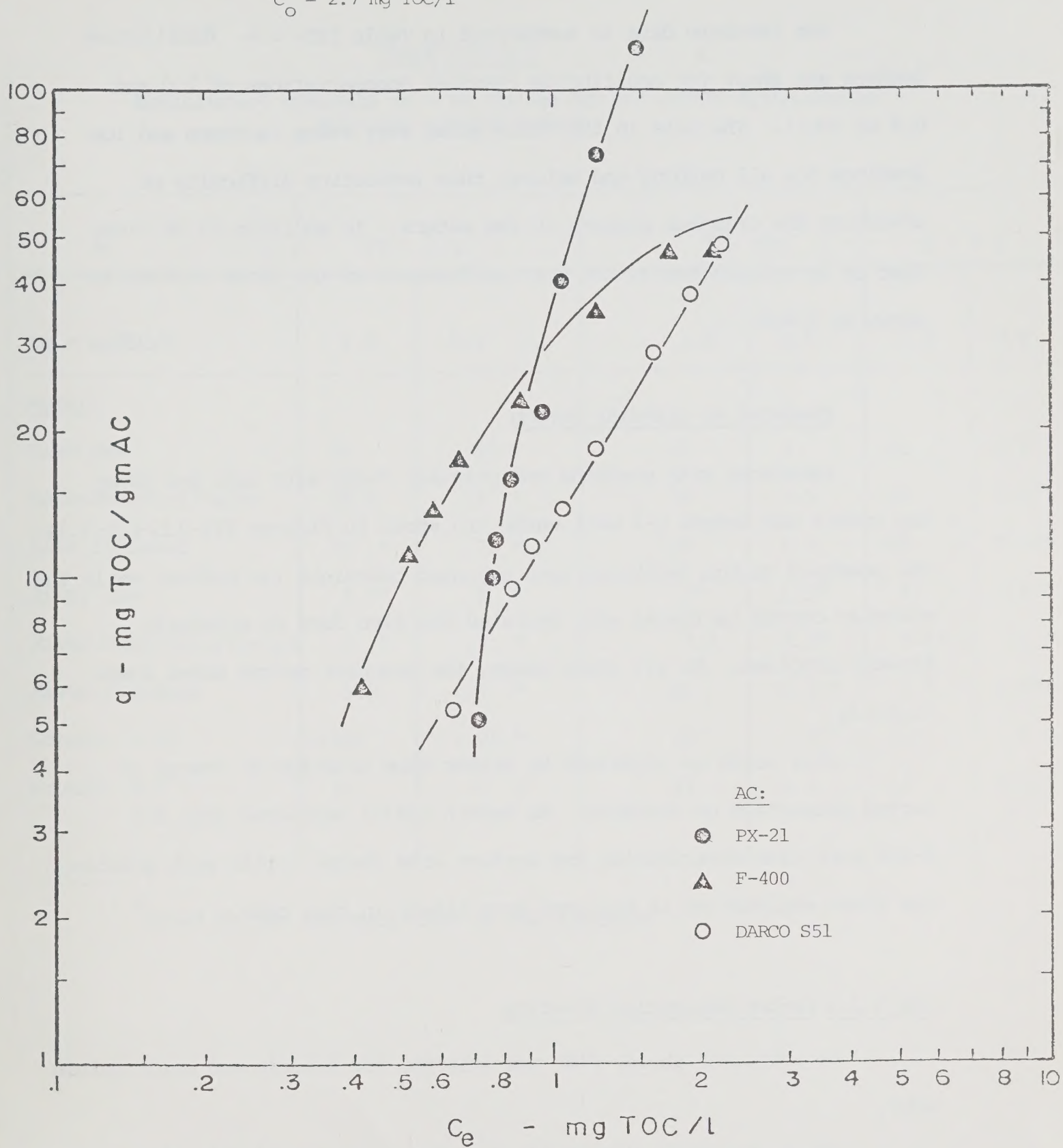


FIGURE III-1.11. ISOTHERMS WITH GROUND G-4 WELL WATER

$$C_o = 2.7 \text{ mg TOC/l}$$



The isotherm data is summarized in Table III-1.5. Equilibrium loadings are shown for equilibrium residual concentrations of 1.0 and 0.4 mg TOC/l. The data in the Table shows very steep isotherm and low loadings for all carbons and waters, thus indicating difficulty of adsorbing the organics present in the waters. In addition it is clear that on an overall basis, the best performance of the three carbons is shown by F-400.

Powdered vs Granular Carbon

Isotherms with powdered and granular F-400 with Lake and River tap waters and Ground G-4 well water are shown in Figures III-1.12-III-1.14. The powdered carbon isotherms were agitated overnight (as before) while the granular carbon isotherms were agitated for five days to eliminate kinetic problems. In all three cases, the granular carbon shows lower capacity.

This could be explained by either slow kinetics or change in carbon properties on crushing. As Rankin (1975) has shown that for F-400 pore size distribution and surface area change little with grinding, the first explanation is believed more likely in this case.

III-1.3.3 Carbon Adsorption Kinetics

As indicated above, F400 was selected for kinetic and pilot column work.

Figure III-1.15 illustrates the adsorption kinetics in three waters. While about 80-90% initial TOC is adsorbed in one day, apparent equilibrium TOC concentration levels were reached in five days.

TABLE III-1.5

EQUILIBRIUM LOADINGS (q - mg TOC/gm AC) AT STATED EQUILIBRIUM
RESIDUAL CONCENTRATION

AC	PX - 2 1		F - 400		S - 5 1	
Ce - mgTOC/ ℓ	1.0	0.4	1.0	0.4	1.0	0.4
<u>Water</u>						
Lake Raw	31	.85 *	21	3	12	2.2*
Lake Prechlorinated	38.5	.1 *	30	3.5	22	2.2*
Lake finished	75 *	.75 *	30	4.3	19	1.35*
River Raw	4.5*	.4 *	7*	1.5*	4*	.8 *
River Superchlorinated	3 *	.1 *	7.4	2.2*	3.5*	.6 *
River finished	5.2	.1 *	11	3.25*	5.2	1.25*
Ground: G-20	>100*	<.01 *	50*	.05*	40*	.1 *
Ground: G-4	32	.1 *	27	4.0	12	2.5 *

* Based on the Extrapolation of the Isotherm

FIGURE III-1.12. ADSORPTION ISOTHERMS WITH LAKE TAP WATER

INITIAL TOC CONCENTRATION = 1.5 mg/l

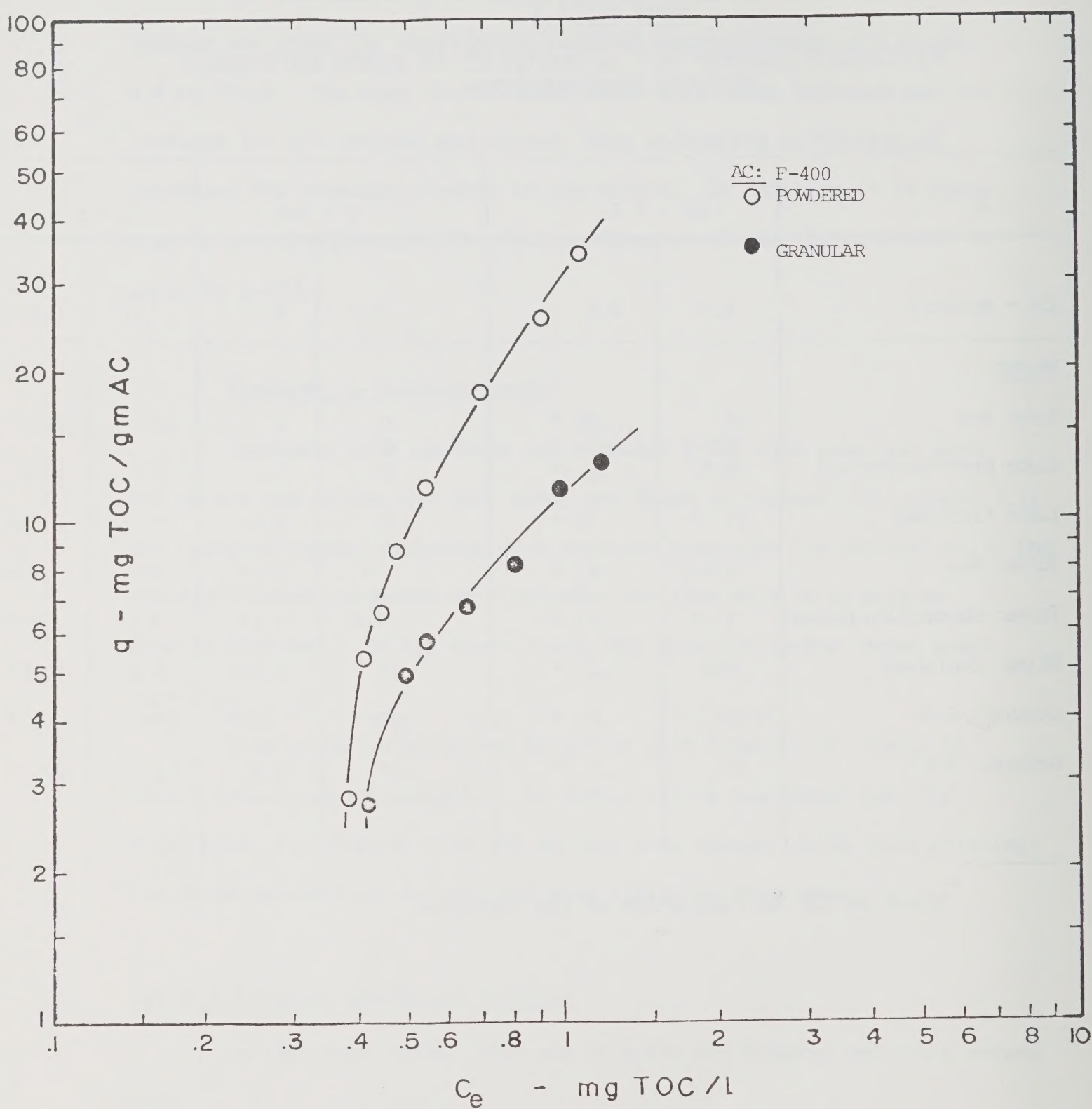


FIGURE III-1.13. ADSORPTION ISOTHERMS WITH RIVER TAP WATER

INITIAL TOC CONCENTRATION = 3.7 mg/l

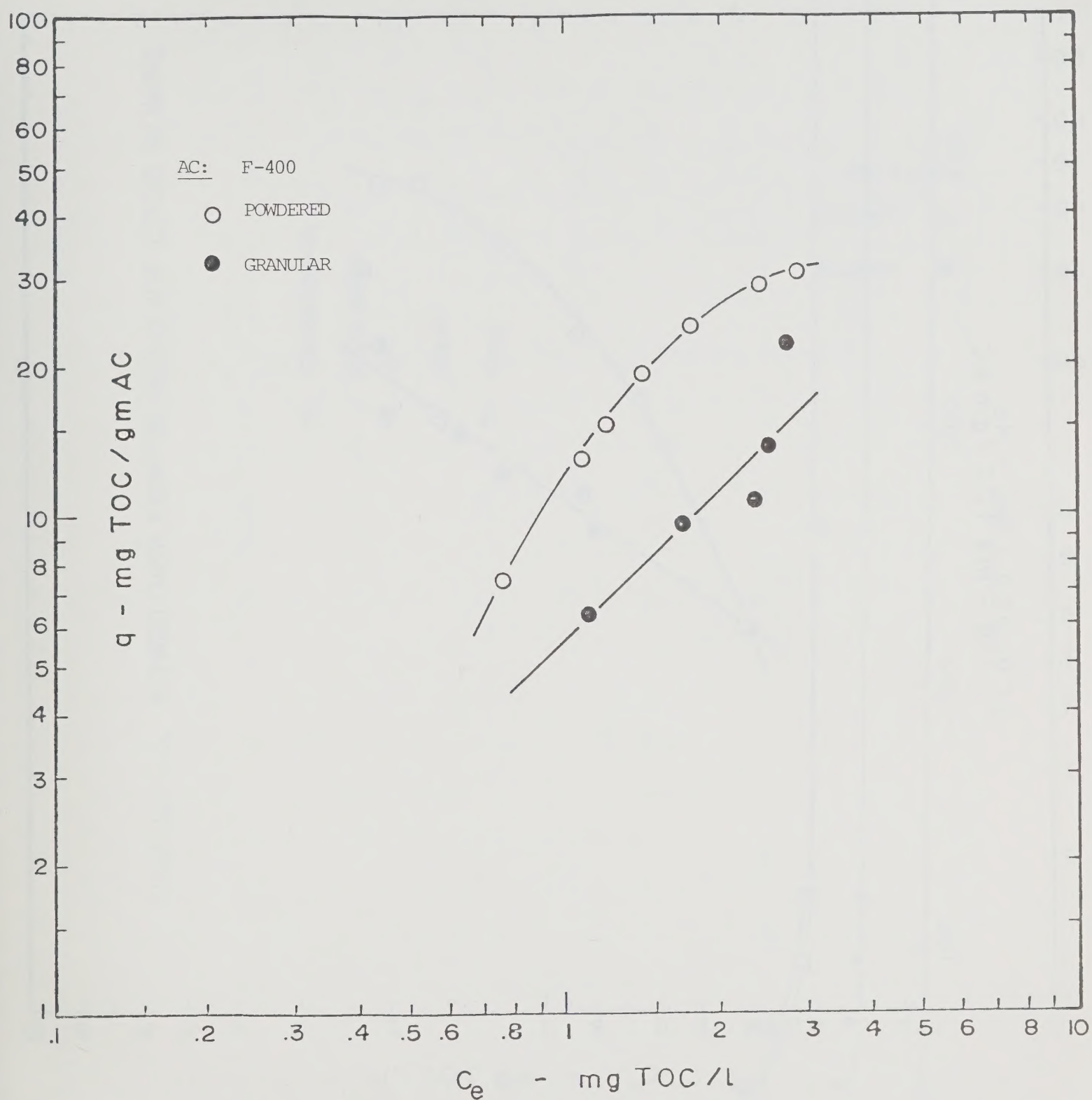


FIGURE III-1.14. ADSORPTION ISOTHERMS WITH GROUND G-4 WELL WATER

INITIAL TOC CONCENTRATION = 2.7 mg/l

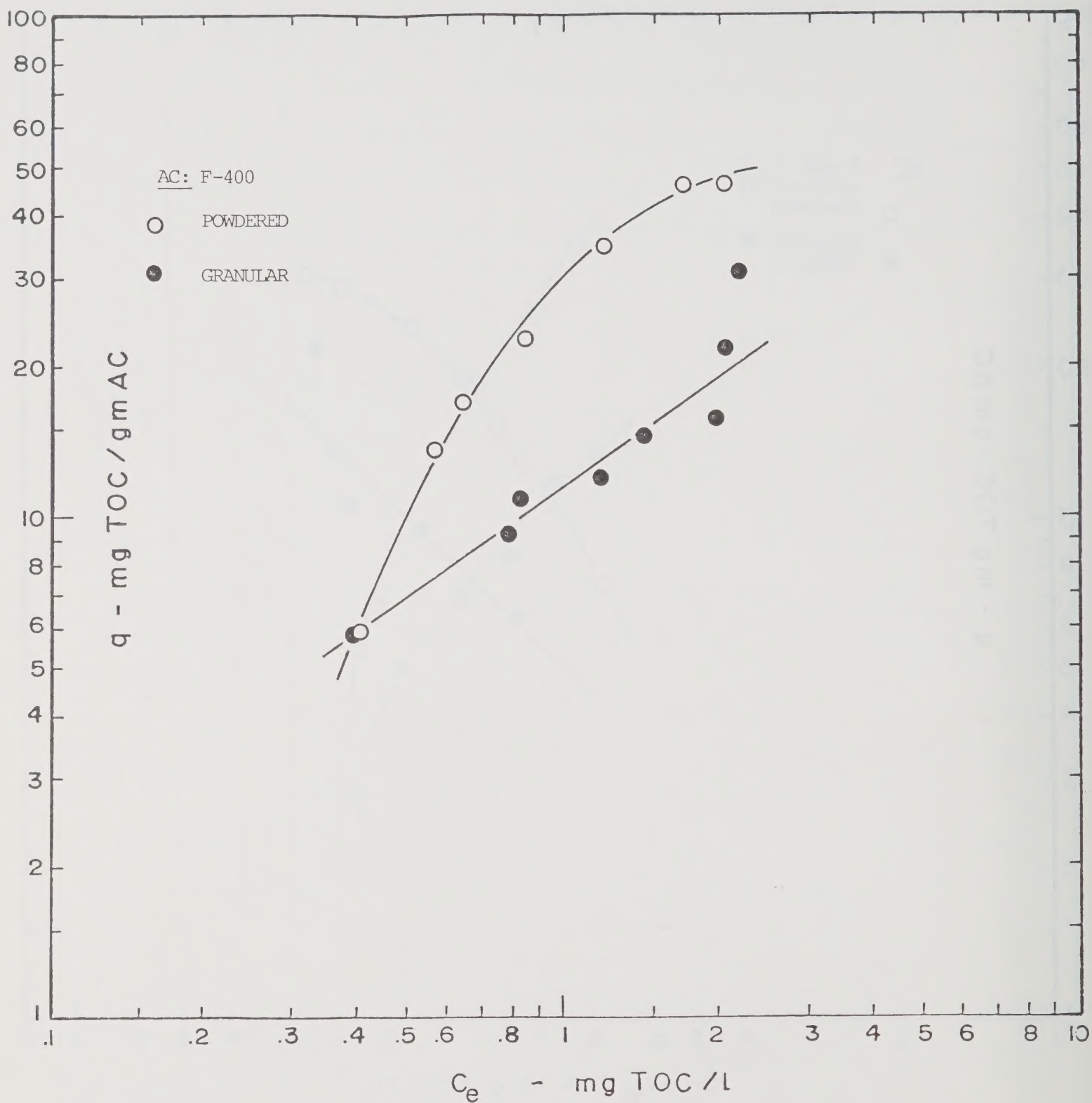


FIGURE III-1.15. ACTIVATED CARBON ADSORPTION KINETICS WITH SELECTED TAP WATERS

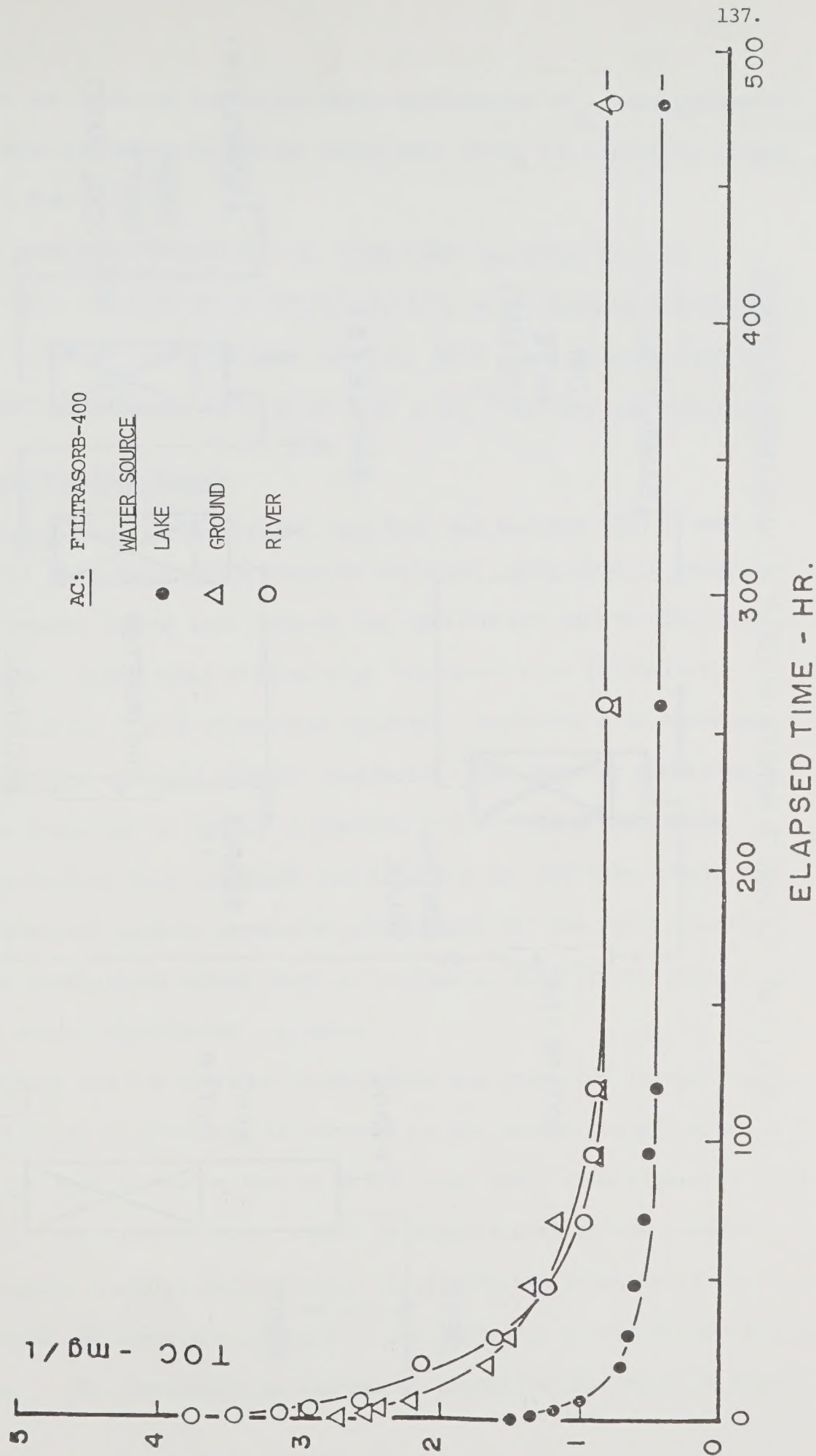
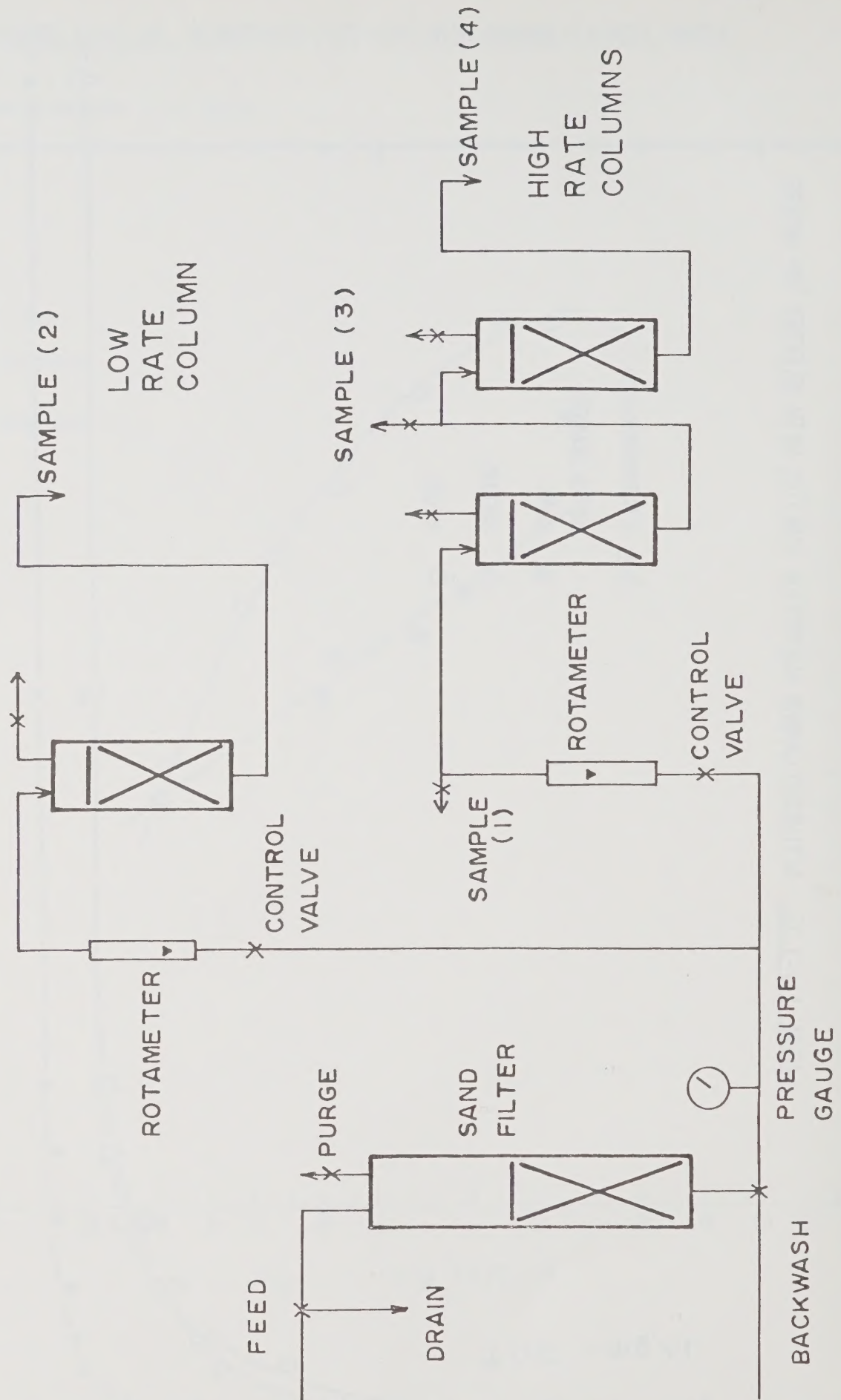


FIGURE III-1.1.16 SCHEMATIC OF McMASTER UNIVERSITY ACTIVATED CARBON PILOT PLANT



From the kinetics curves, particle diffusivity (D_p), the parameter indicating adsorption rates, can be calculated using the equations listed in Section I-2.6.

The particle diffusivity, D_p , with Lake tap water is $1.16 \times 10^{-10} \text{ cm}^2/\text{sec}$. This value is relatively low, as at Morsang sur Seine, France, $D_p = 2.8 \times 10^{-9} \text{ cm}^2/\text{sec}$ (see Benedek, 1977), was obtained and in Viry Chatillon, France, a value of $3.82 \times 10^{-10} \text{ cm}^2/\text{sec}$ was obtained.

III-1.3.4 Breakthrough Curves

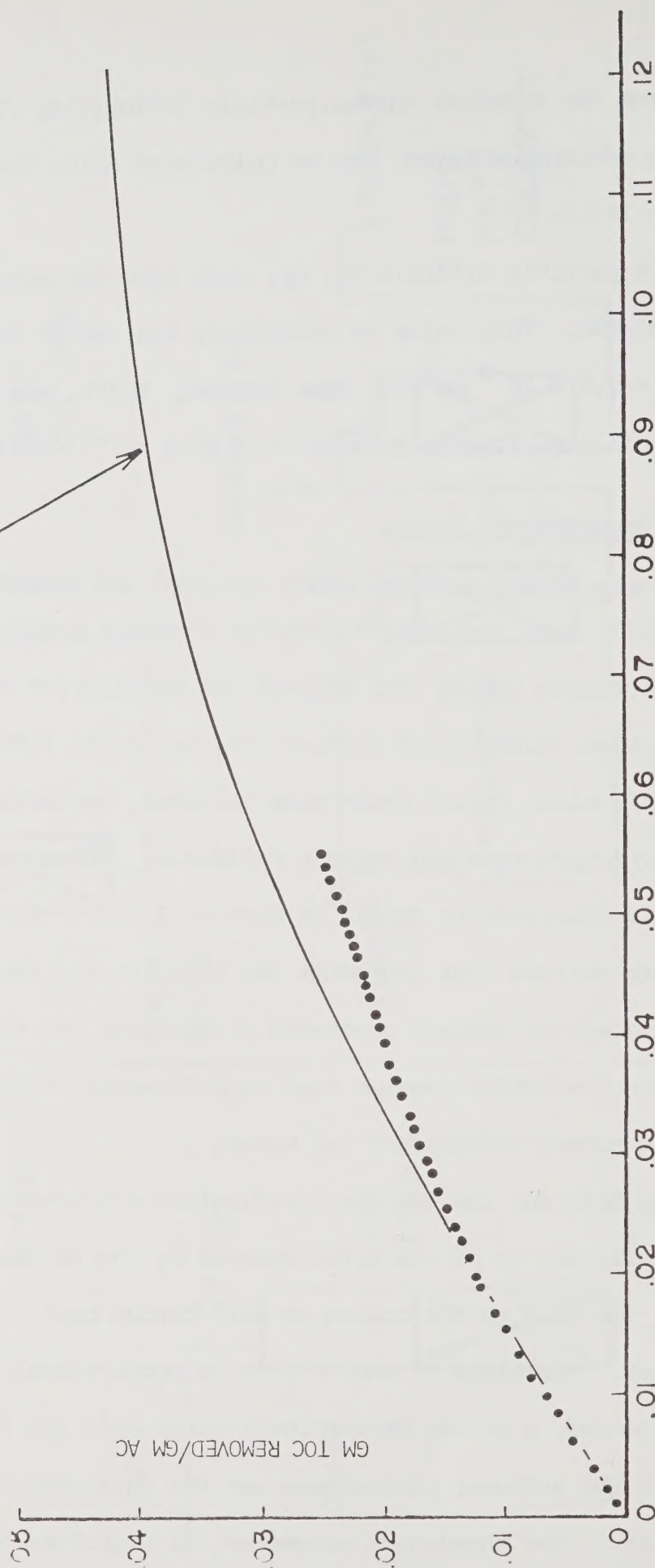
Maqsood and Benedek (1977) and Peel and Benedek (1977) and Benedek (1977) have developed a computer assisted prediction of carbon column performance taking into account the equilibrium carbon adsorption, feed properties, bulk liquid diffusivity, bacterial film diffusivity, particle diffusion, liquid phase mass transfer, bacterial film thickness, bacterial reaction rate and organic residuals. The computer modelling procedure is described in detail in Section I-2.6. Using the proper coefficients derived from isotherms and kinetics for the Lake supply tap water, the computer package generated predictions for the pilot plant. The computer predictions assume that no biological activity is present as the feed is normal disinfected tap water.

The data and the computer predictions are presented in two forms. First, cumulative, by plotting TOC removed by the carbon column versus the gms of TOC feed to the column on unit carbon basis (see Figure III-1.17 for example). The slope of such a plot is proportional to the percent removal. Second, a column breakthrough curve with the fraction of the feed TOC in the effluent plotted against the parameter Z (see Figure III-1.18, for example). The throughput parameter, Z , signifies the ratio of total

FIGURE III-1.17. CUMULATIVE TOC REMOVAL

20 cm bed depth
Filtered TOC = 1.24 m/h Feedrate

COMPUTER PREDICTION

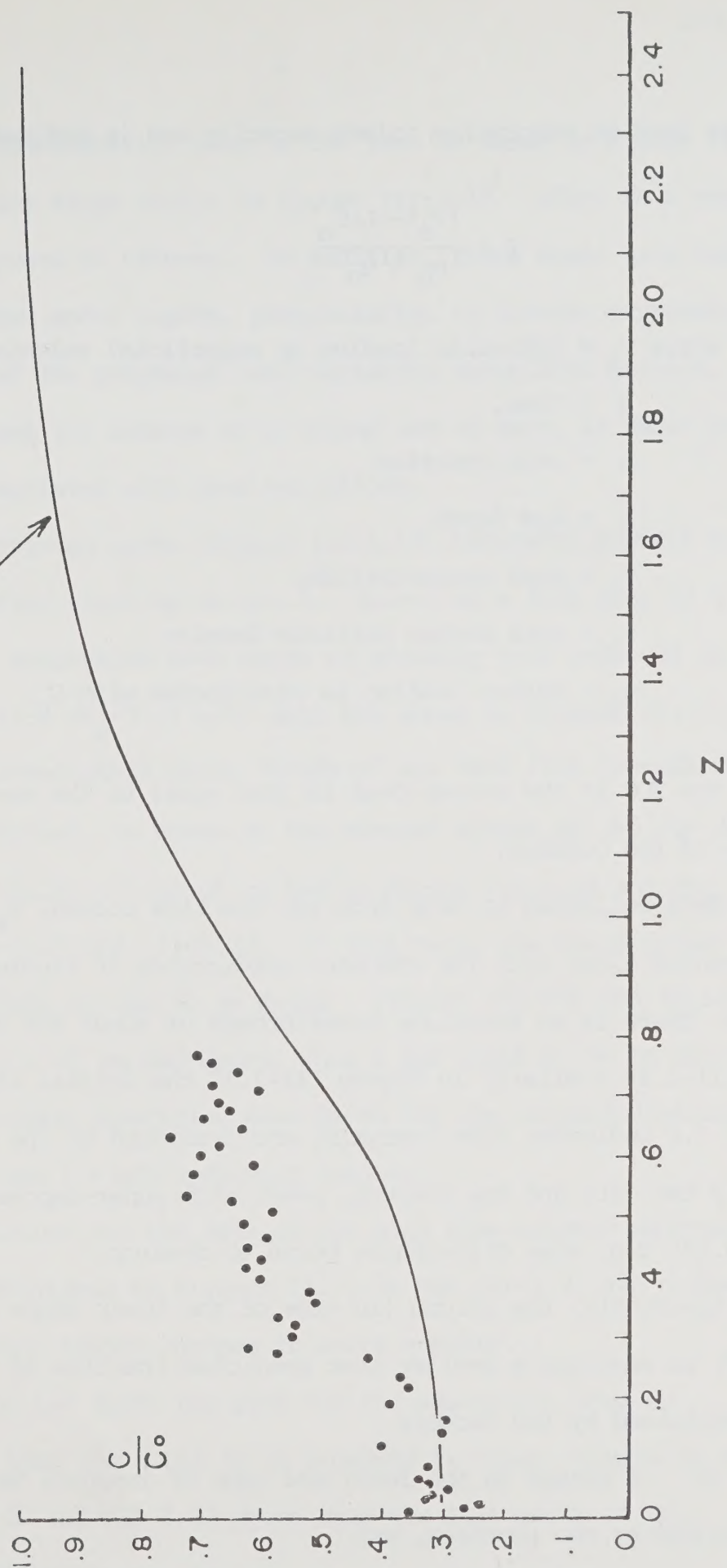


GM TOC APPLIED/GM AC

FIGURE III-1.13. COLUMN BREAKTHROUGH

20 cm depth at 1.2 m/h Feedrate

COMPUTER PREDICTION



substrate feed to adsorptive column capacity and is defined as

$$Z = \frac{(V_s t - \varepsilon L) C_o}{\rho_b L q_o} \quad (2)$$

where V_s = hydraulic loading or superficial velocity,

t = time,

ε = void fraction,

L = bed depth,

C_o = feed concentration,

ρ_b = bulk carbon particle density

q_o = carbon loading in equilibrium with C_o .

At $Z=1$, the TOC in the column feed is just equal to the maximum adsorptive capacity of the columns.

Data collected to date from the low flow column, $V_s=1.24$ m/h, are presented along with the computer predictions in Figures III-1.17 and III-1.18. There is an immediate breakthrough of about 30% of the feed shown in Figure III-1.18 similarly in Figure III-1.17 the initial slope is about .7, a slope of 1.0 indicates 100% removals, and predicted by the isotherms. Initially the data and the computer prediction super-impose but at a TOC of 0.025 g/g, some differences begin to develop.

Apparently, the column (in view of the lower slope in Figure III-1.17) is removing a smaller than predicted fraction of the feed. This may be explained by two factors

- (i) a change in the level and type of organics in the feed from those assumed by the isotherm, and
- (ii) differences between estimated and actual mass transfer or equilibrium factors.

The high concentration wave in the feed as shown in Figure III-1.19 corresponds to a low slope region in Figure III-1.17. After this wave passes, removal appears to recover. In addition, there could have been some errors in other model inputs, particularly, in kinetic expressions. However, in view of the potential feed variation associated problem, as discussed above, and the success of a second set of data, as shown below, it is probably associated with feed variations.

The breakthrough curve (Figure III-1.18) indicates gradual breakthrough shortly after start-up at $Z=0.2$. Hence, at a feed rate of 1.2 m/h, the apparent adsorption wave depth is probably just under 20 cm.

The high flow ($V_g=7.37$ m/h) data are shown in Figures III-1.20 - III-1.23. Again immediately about 30-40% of the feed (the non-adsorbable residual) broke through, as shown by the removal slopes of .65 for 20 cm bed in Figure III-1.20, .7 for 40 cm bed in Figure III-1.18 and C/C_0 of about .4 in Figures III-1.22 and III-1.23. In this case, the breakthrough is essentially immediate at the 20 cm depth (Figure III-1.19) and follows quite rapidly at the 40 cm bed depth. Thus a bed depth of 40 cm appears to be near the minimum adsorption wave depth (or the suggested minimum filter depth) at the 7.4 m/h hydraulic loading.

The prediction and the data of the high flow columns superimpose and the slight deviations in Figures III-1.20 and III-1.21 are probably due to the relatively minor random changes in water quality.

The carbon bed depth required for the adsorption wave is slightly greater than the total 40 cm provided by these columns as shown in Figures III-1.20 and III-1.23 where only the last parts of the characteristic "S"-shape are present.

FIGURE III-1.19. PILOT CARBON COLUMN FEED AND EFFLUENT TOC CONCENTRATIONS. ($V_s = 1.2$ M/H; CARBON BED DEPTH = 20 CM).

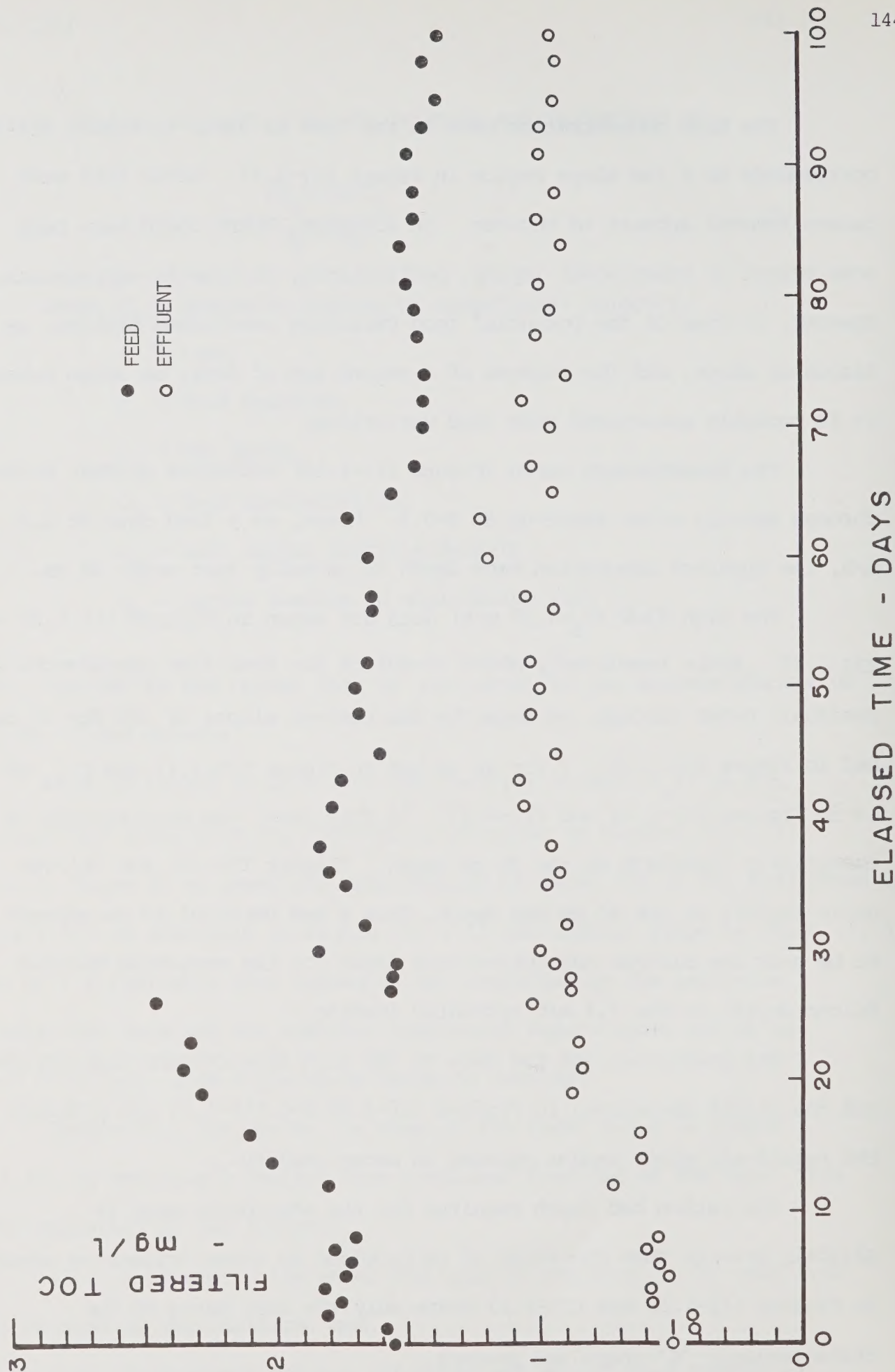


FIGURE III-1.20. CUMULATIVE TOC REMOVAL

20 cm bed depth
Filtered TOC = 7.4 m/h feed rate



GM TOC APPLIED/GM AC

FIGURE III-1.21. CUMULATIVE TOC REMOVAL

40 cm bed depth
Filtered TOC = 7.37 m/h feed rate

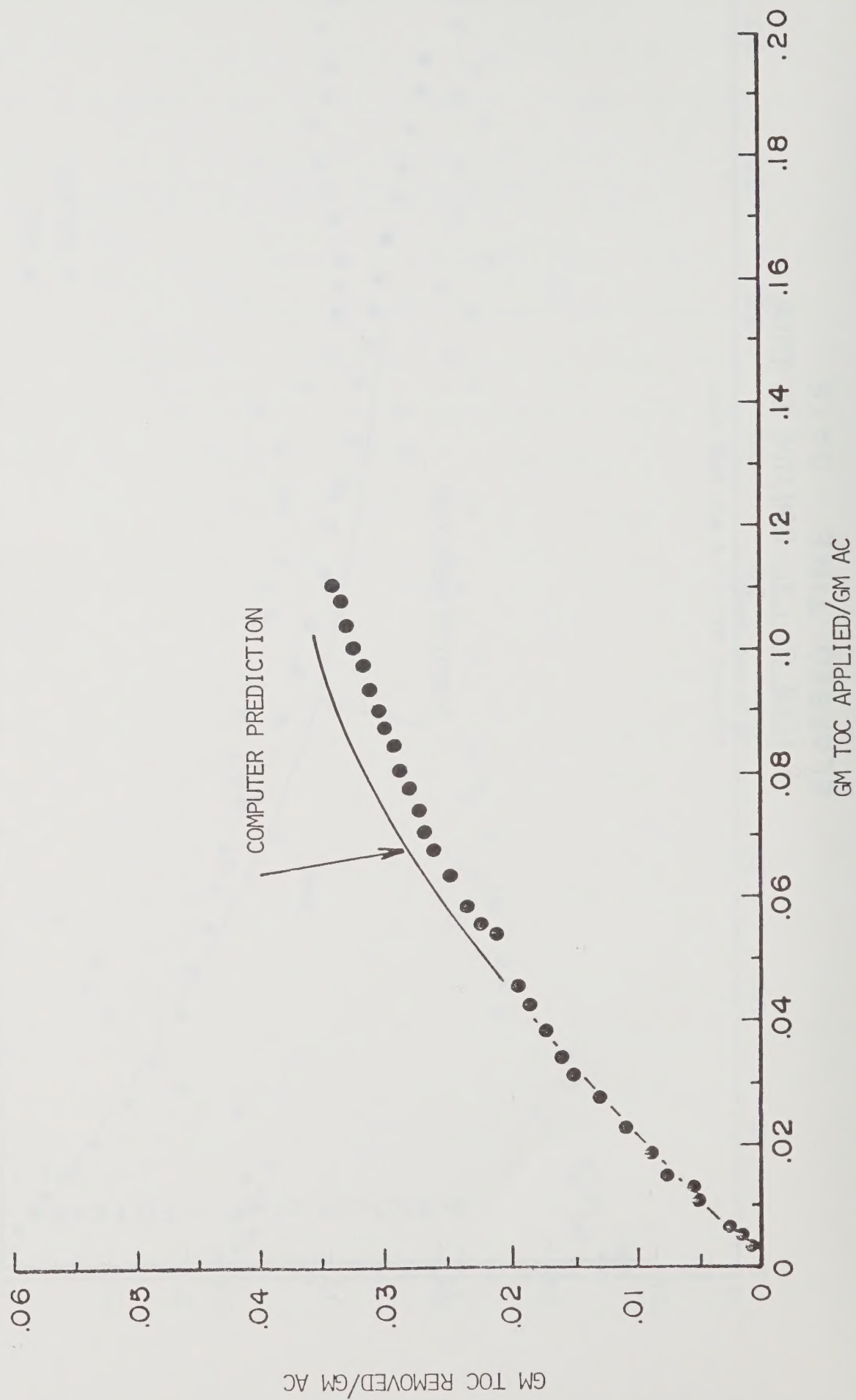


FIGURE III-1.22. COLUMN BREAKTHROUGH

20 cm depth at 7.37 m/h Feedrate

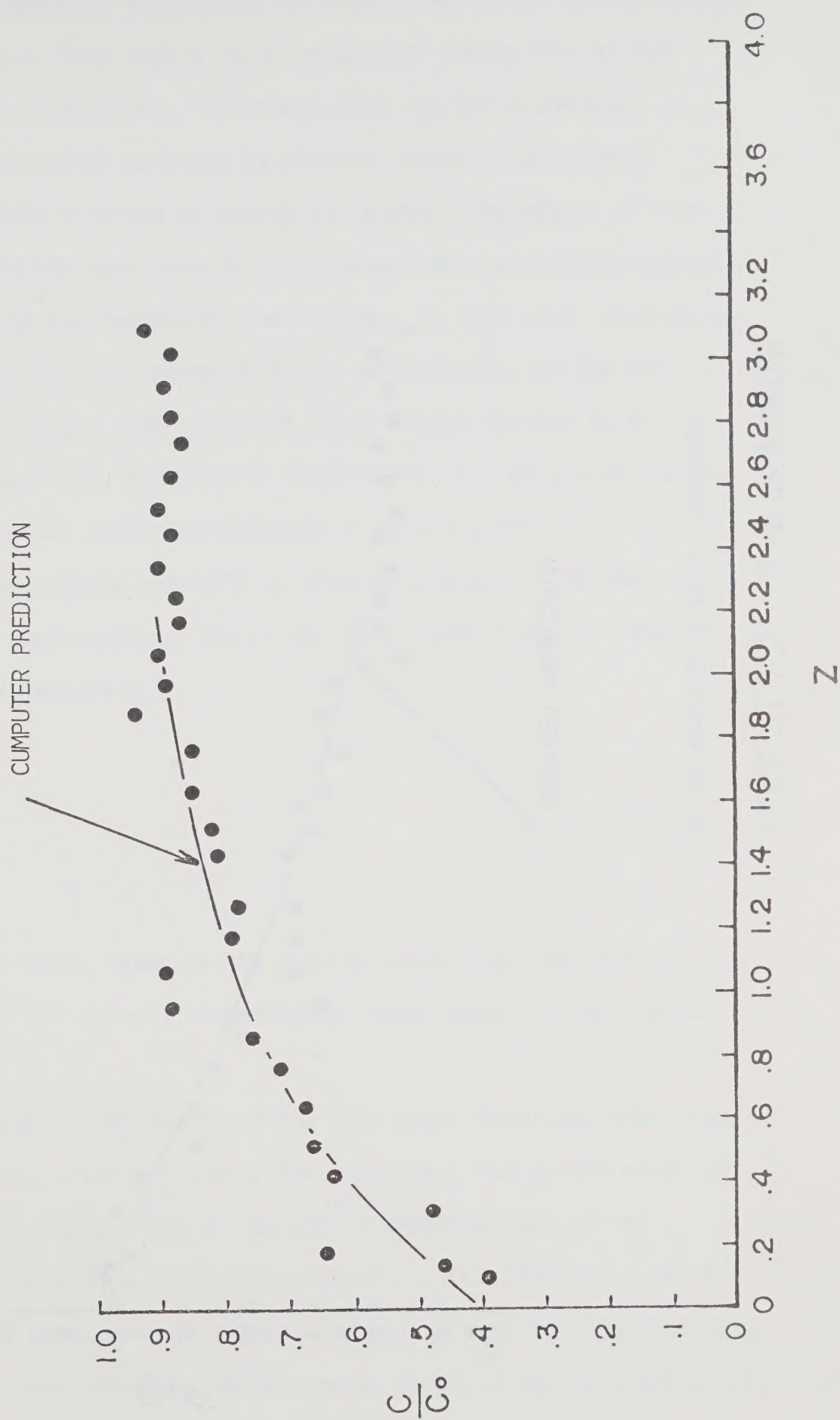
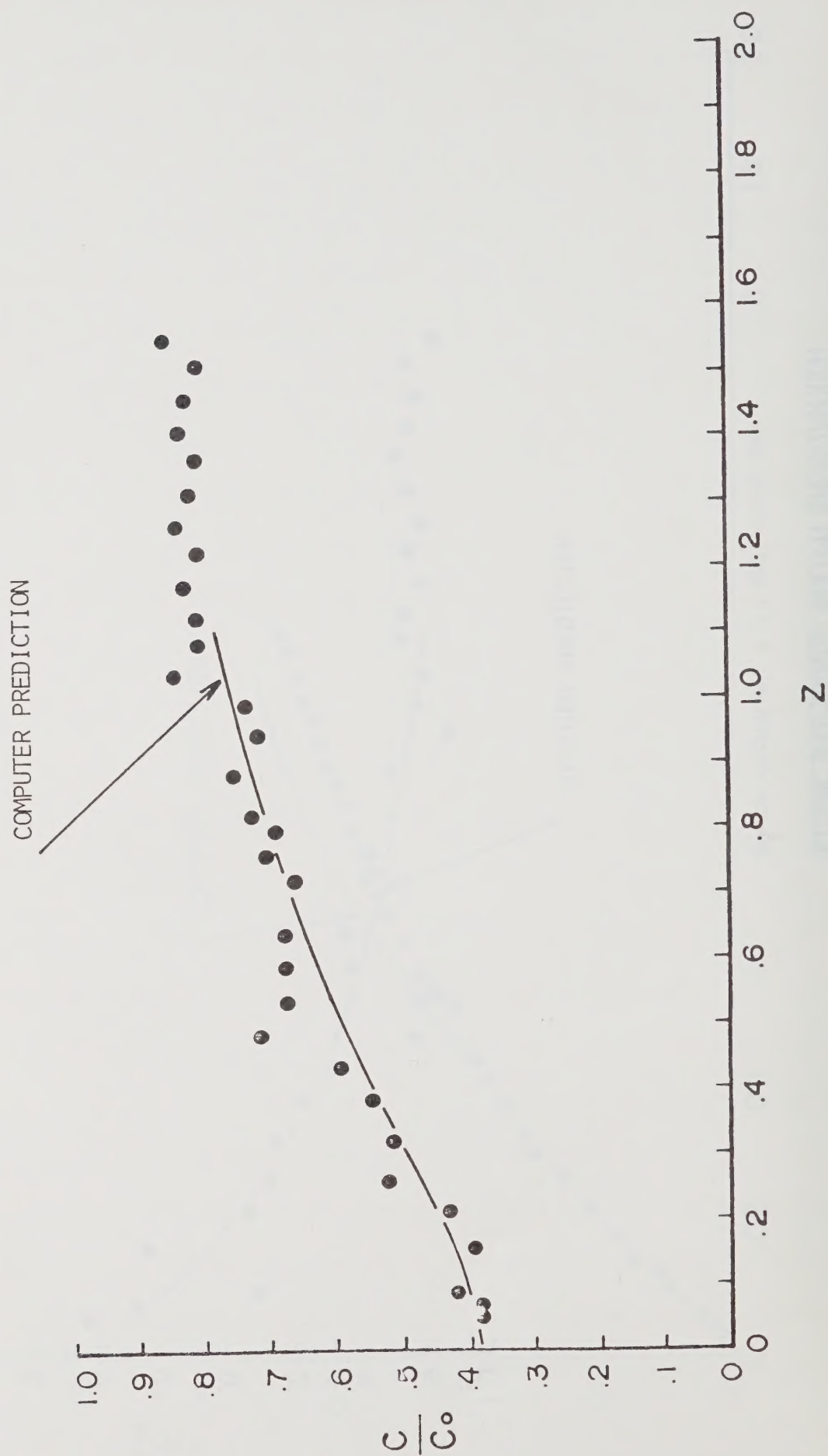


FIGURE III-1.23. COLUMN BREAKTHROUGH

40 cm depth at 7.37 m/h Feedrate



All of the computer simulations assumed a negligible biodegradation rate. This appears to have been a valid assumption during the initial operating period as if anything, the actual data was below computer predictions. If biological activity is present, removals are always increased beyond those obtained by adsorption alone. The effect of biological activity becomes most pronounced, however, when adsorption ceases and biodegradation is the predominant mechanism. In such case, cumulative removal curves level off to a constant slope corresponding to the biodegradation in the filter. Such constant slope region appears to be developing in Figure III-1.18 beyond an applied TOC of 0.08 g/g of carbon. On Figure III-1.19, this region corresponds to data beyond $Z=2.0$, a point where most of the adsorptive capacity is usually exhausted. On the basis of Figure III-1.19 approximately 10% of the feed organics may be removed on the long term biologically.

III-1.4 SUMMARY

Three different water plants drawing water from Lake Ontario, the Grand River and the ground, respectively, were chosen for adsorption studies.

In the case of the river and the lake water supplies, conventional treatment removes approximately a $\frac{1}{4}$ of the organics. The ground water is presently untreated. Adsorption is capable of removing most of the remaining organics down to a total organic carbon (TOC) level of 0.3-0.4 mg/l. The level of total organic chlorine was .1-.9 mg/l for the lake water supply, .3-1.2 mg/l for the river water supply, about .3 mg/l for the ground water

supply. The TOC level increased upon the chlorination during treatment.

PAH levels of about 1.2 $\mu\text{g/l}$ was found in the lake water, and about 0.6 $\mu\text{g/l}$ in the ground water.

Adsorption capacity of the carbon depends on carbon and water characteristics. With F-400 maximum equilibrium adsorption capacity of 50-80 mg TOC/gm AC was achieved.

Adsorption kinetics of the lake finished water is slow.

A computer model is able to predict pilot carbon column performance quite well.

III-1.5 REFERENCES

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APPENDIX A

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APPENDIX B

PLANT VISIT REPORTS

PLANT VISIT TO
LENGG POTABLE WATER TREATMENT PLANT
OF THE CITY OF ZÜRICH, SWITZERLAND

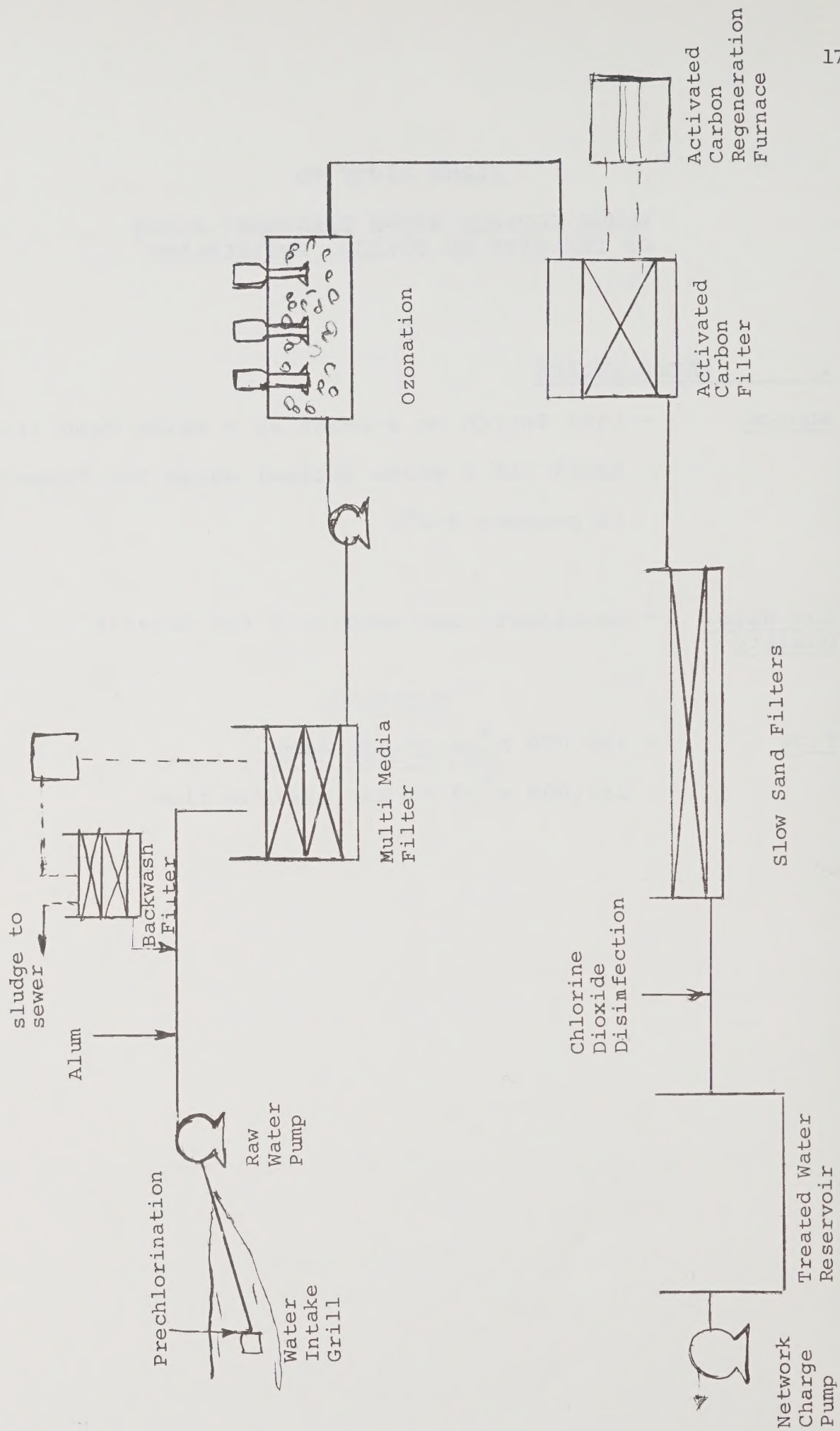
1. WATER INTAKE

Source - Lake Zurich at a point 32 m below mean lake level (16 m above bottom) where the temperature is between 3-8°C

Raw Water Quality - Excellent, see section 3 for details

Flow - 180,000 m³/d on average
250,000 m³/d is the maximum flow

2. PLANT FLOWSHEET



3. WATER QUALITY PARAMETERS

The table below is based on average of one set of readings per week over the three week period stretching from February 2, 1977 to March 1, 1977.

	pH	DOC as C mg/l	KMn O ₄ as O ₂ mg/l	UV Extinction E _{10 cm} E _{254 mm}	Turbidity E _{10 cm} E _{420 mm}
Raw water	7.75	1.5	1.2	.31	0.26
Raw water after prechlor.	7.76	1.5	1.1	.27	0.26
Multi Media Filter Effluent	7.73	1.4	1.1	.24	0.13
Ozonation Effluent	7.71	1.4 ⁻	0.85	.14	0.9
Activated Carbon Effluent	7.70	1.1	0.7	.12	0.7
Slow Filter Effluent	7.73	1.1	0.7	.11	0.7
Treated Water Reservoir	7.85	1.1	0.7	.11	0.6

In 1974, an extensive analysis of organic matter in water was undertaken. The results of this analysis, however, are only marginally applicable as the ozonation and activated carbon adsorption step was not yet included. A summary of the results are shown below:

	<u>Raw</u>	<u>ug/l</u> <u>Prechlorinated</u>	<u>Treated</u>
<u>Polycyclic Aromatic</u> <u>Hydrocarbons (PAH)</u>			
Total PAH	23.6	34.7	24.9
Fluoranthene	16.7	24.5	20.0
3-4 Benfluoranthene	3.0	4.8	2.2
3-4 Benzpyrene	0.9	0.8	0.5
1.12 Benzpyrene	1.1	1.3	0.7
11.12 Benzfluoranthene	1.0	1.6	0.8
Indenopyrene	0.9	1.7	0.8
<u>Pesticides</u>			
Total Pesticides	2.8		2.1
DDT incl. PCB	2.0		1.3
DDE " "	0.3		0.4
Lindane	0.2		0.2
Dieldrin	0.1		0.1
Aldrin	nf		nf
Thiodane α	0.1		tr
Thiodane β	tr		0.1
HCH α	tr		tr
HCH β	tr		tr
MCH δ	tr		tr
HCB	trace		0.1
Total chlorinated material	2.8		2.4
Pure DDT	tr		0.1
Pure DDE	0.2		0.2
Aophen A60	2.1		1.9

4. PROCESS DETAILS

4.1 Prechlorination

Injection Point - At water intake from lake

Dosage - 1 mg/l in summer, 0.3 mg/l in winter
of gaseous chloride

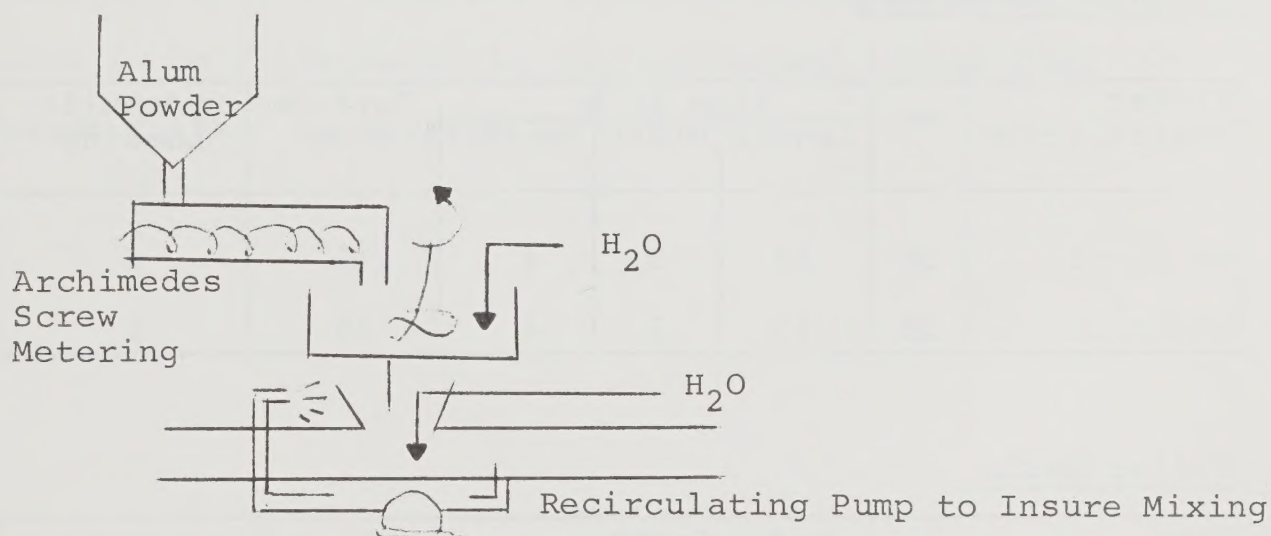
Purpose - To avoid problems with mollusc larvae
(migratory muscles)

4.2 Coagulation

Injection Point - In raw water, channel just ahead of dual
media filters

Dosage - 1-2 mg/l of alum (as $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$)

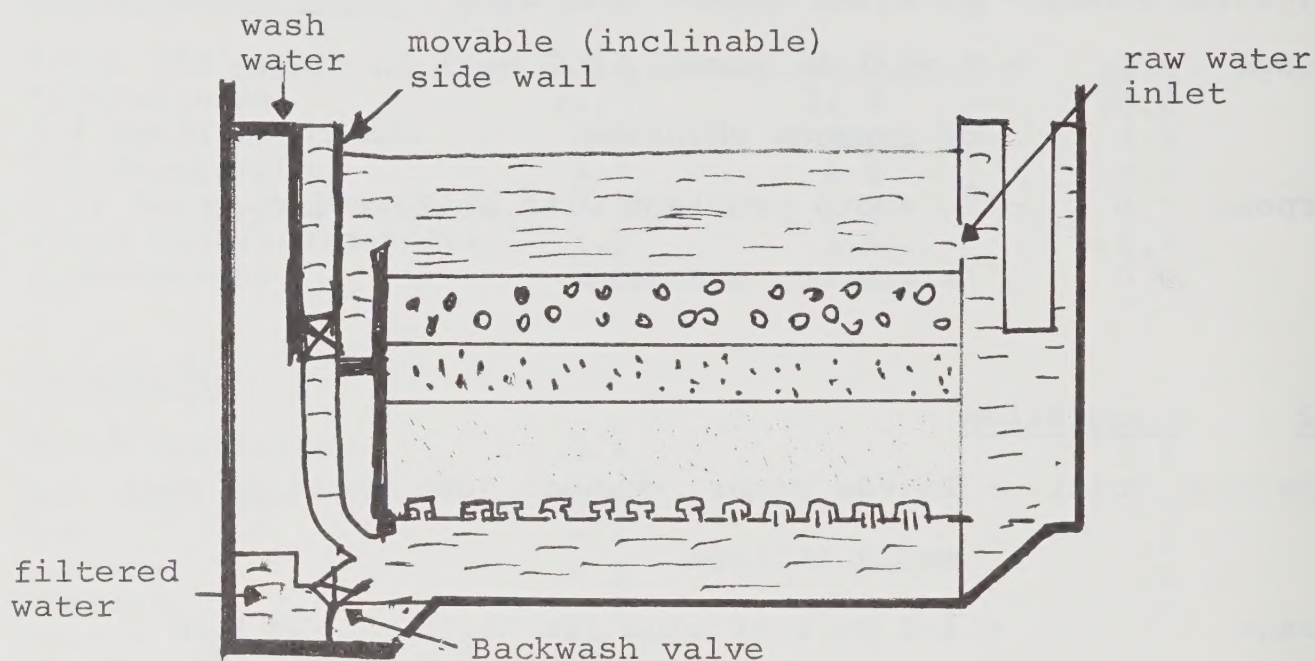
Preparation



4.3 Flocculation

Activated Silica can be added just ahead of the multi-media filters, however, its use has not been found necessary. The method of addition is the same as that of the alum and the optimum dosage is believed to be 10% of the alum dosage.

4.4 Multimedia Filtration (Filter Supplier - Sulzer)



Process Parameters

Filter Installation	NO	Size in m			Surface Area	Hydraulic Loading m/h
		Length	Width	Depth		
Original	20	15	3	4	45	6
Addition	20	15	3	4	45	6

Filter Media

Type (in direction of downward flow)	Media Depth		Size Distribution mm
	Original	Addition	
Pumice	50	40	0.7-1.0
Anthracite	--	30	
Quartz Gravel	70	70	

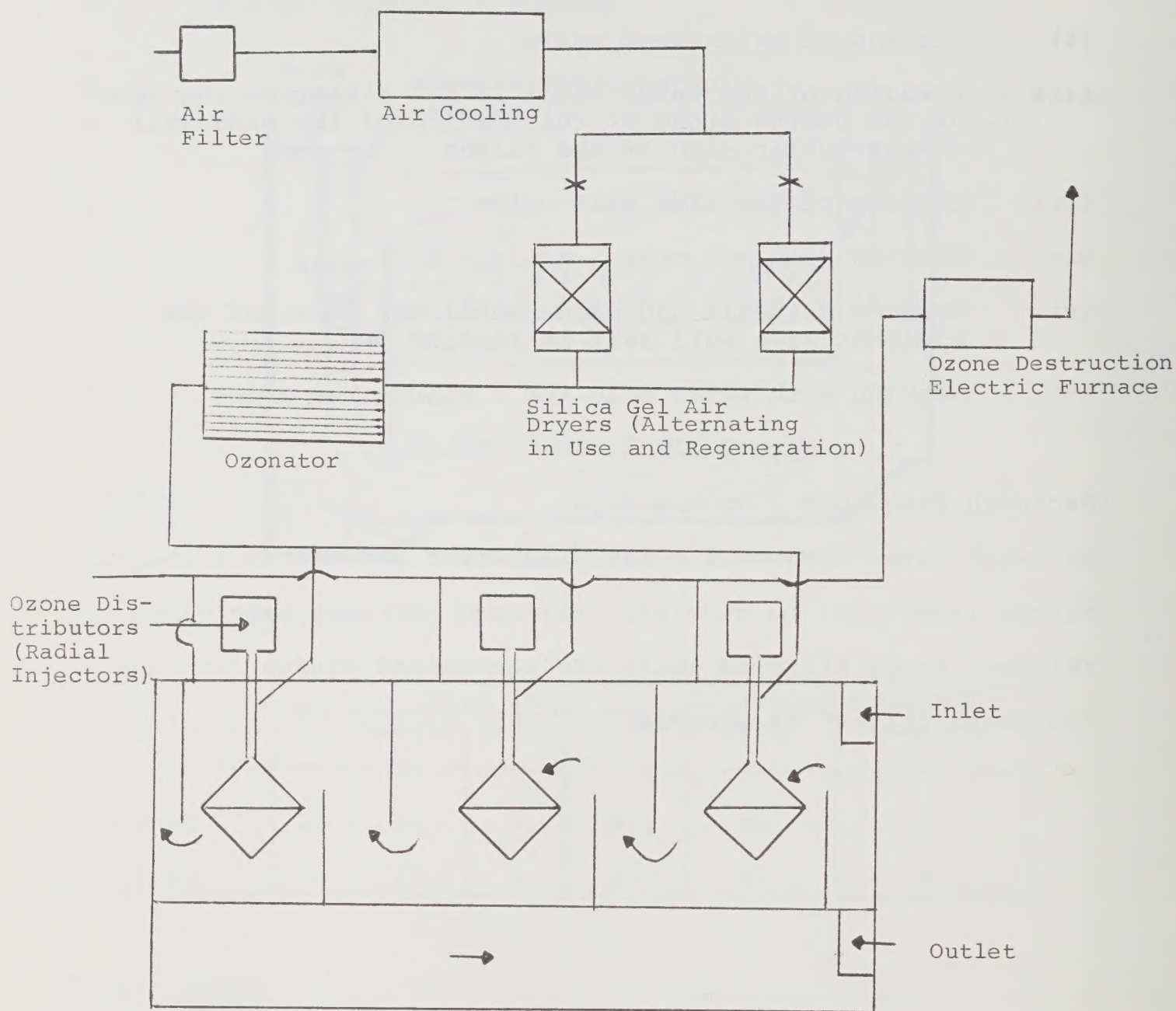
Filter Backwash Steps

- (i) Closing of water feed valve
- (ii) Lowering of the water level in the filter to the level of the pumice stone by the opening of the side wall on the outlet side of the filter
- (iii) Closing of the side wall valve
- (iv) Washing with air only 2 m/h for 2 minutes
- (v) Washing with air and water until the level of the effluent side wall weir is reached
- (vi) Washing with water only for 2 minutes at 2 m/h

Backwash Frequency - once/4 days

Backwash Water Treatment - Backwash water is sent to a special filter (identical to others). Filtered backwash water is returned to be filtered while the backwashed sludge from the "backwash filter" is sewerred.

4.5 Ozonation



Supplier of Ozonators - Kerag

FLWSHEET OF OZONE PREPARATION AND ADDITION

Dosage - $1.25-3 \text{ g/m}^3$

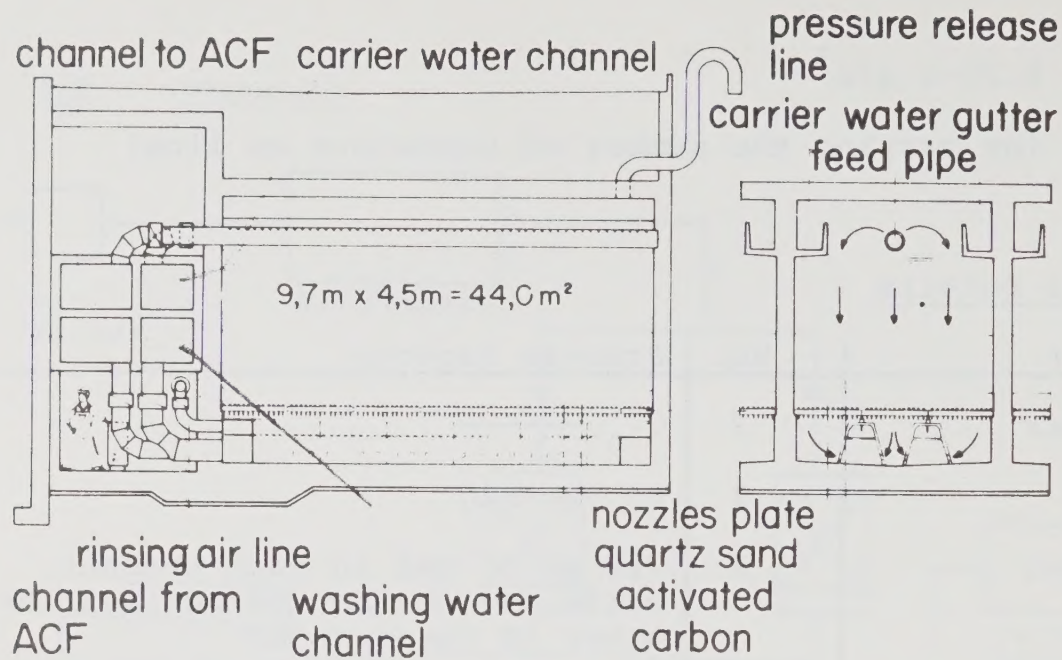
(by varying the number of ozonators on line)

Equipment Details

<u>Equipment</u>	<u>No.</u>	<u>Process Aspects</u>
Air Filter	2	-----
Predrier	2	By cooling
Silica gel Drier	2	730 kg of gel in each chamber, while one chamber is on-line the other is regenerated
Ozonators	6	32.5 kg/ozonator
Reaction Basin	2	465 m^3 in volume, therefore, minimum detention time is above 5 minutes
Ozone Destruction Furnace	2	By electric heat at or above 280°C

4.6 Adsorption by Activated Carbon

In addition to the granular carbon filters, there are facilities to add up to 1,000 mg/l of powdered carbon in case of an emergency. In view of the fact that the addition of powdered carbon has not been practiced since the installation of the granular carbon filters, the discussion below will be restricted to these filters.



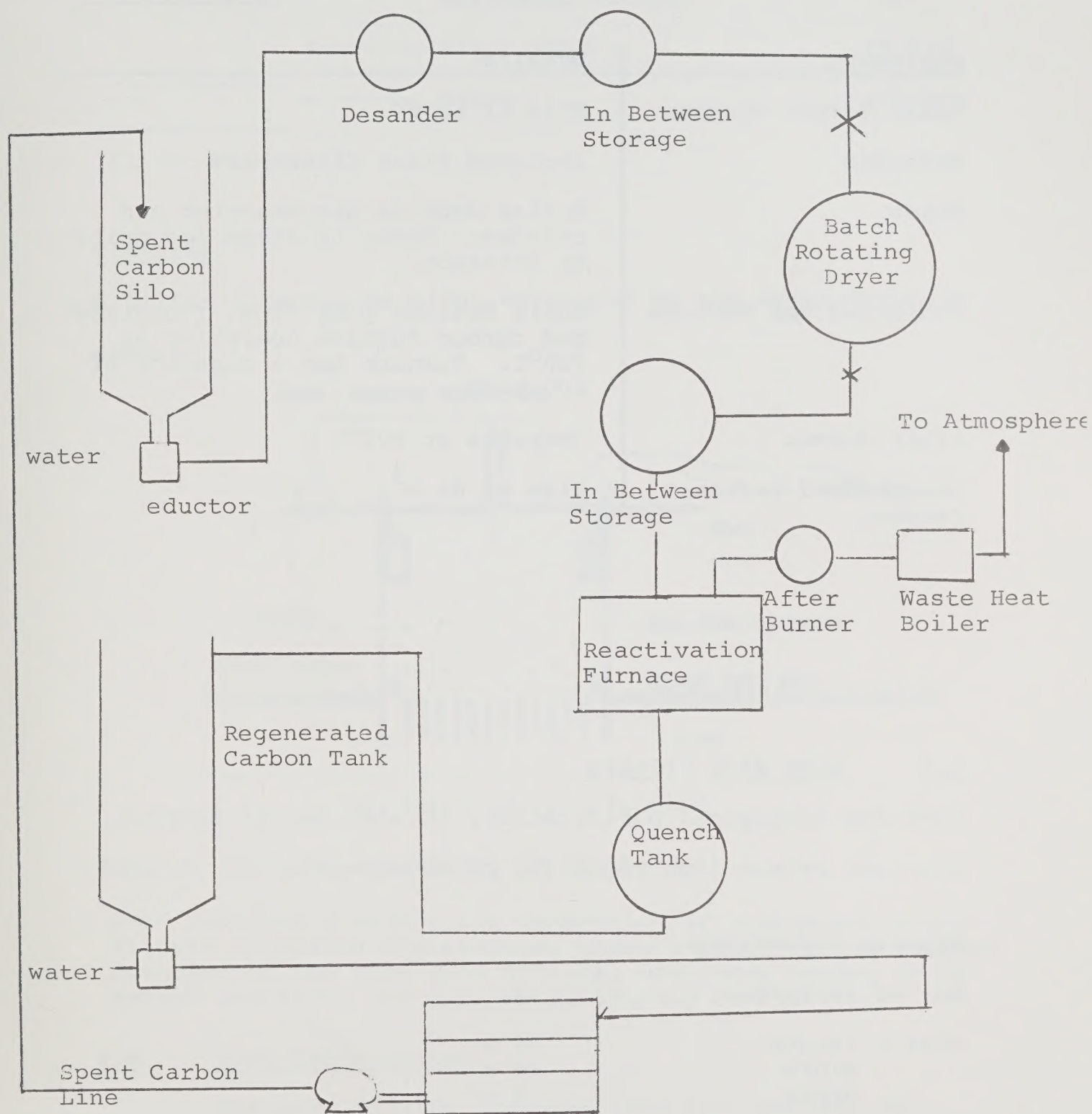
Lengg lakewaterworks; Profile and cross-section of an activated carbon filter

Process Parameters

No. of filters	12
Size - Depth	5.8* m
Width	4.5 m
Length	9.7 m
Surface/filter	44 m ²
hydraulic loading	24 m/h
<u>medium</u> - Activated Carbon	
Type	Norit Row 0,8 cylindrical
Size - Length	1.5-4 (avg. ≈ 2.5) mm
Diameter	0.8 mm
Depth in filter	0.70 m
Superficial Residence Time	1.75 m/h
<u>Sand</u>	
Size	
Depth in Filter	0.50 m

Backwash Methods

Exactly as for multimedia filter, except for frequency, which is twice per week.

4.7 Activated Carbon Regeneration

Process Parameters

Transportation of carbon is based on water eduction

Equipment	Details
Spent Carbon Storage	Silo of 80 m ³
Desander	Inclined Plane Classifier
Dryer	Entire drum is disconnected and rotates. Dryer is steam fed prior to rotation.
Fluidized Bed Furnace	Norit Design, plug flow, fluidized bed carbon furnace operating at 700°C. Furnace has a capacity of 100 kg/h
After Burner	Operates at 900°C
Reactivated Carbon Storage	Silo of 80 m ³

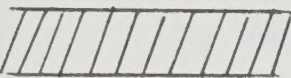
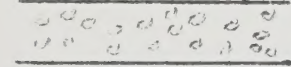
4.8 Slow Sand Filters

Used for biological purification, it also serves to precipitate excess lime added for pH adjustment.

Process Parameters

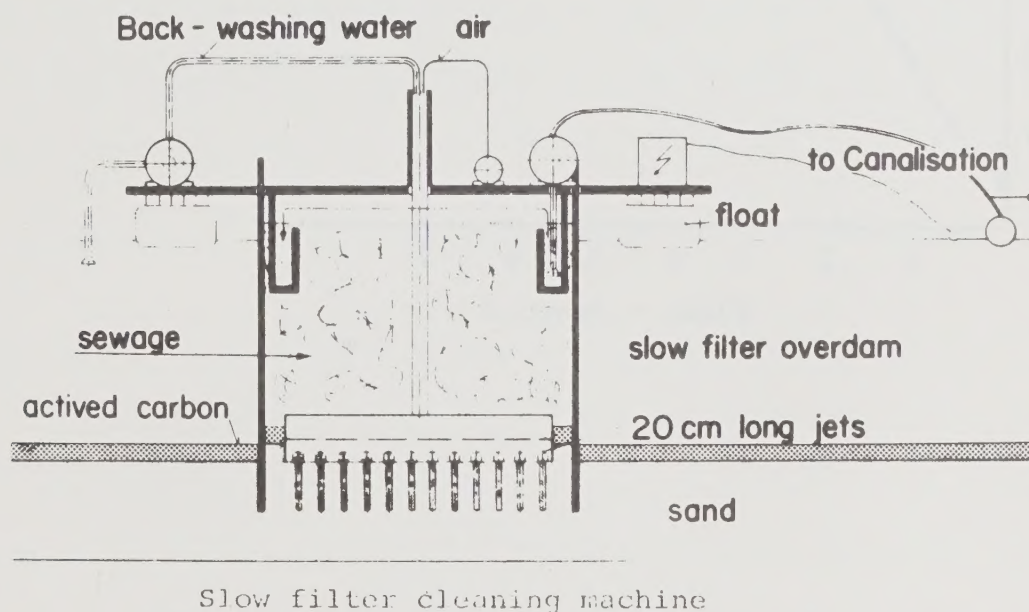
No. of filters	14
Size - length	48 m
width	24 m
depth	4 m
Surface Area per Filtre	1.20 m ²
Superficial Velocity	0.67 m/h

Medium

	<u>Type of Material</u>	<u>Depth</u> cm
	Activated Carbon*	10
	River Sand	50-100
	Gravel	unknown
Filter Floor		

Cleaning

A filter cleaning machine, developed by the Water Works is used.



Sand is replaced once every 10-20 years.

* Used previously before the compaction of activated carbon filters to insure disinfectant elimination. In the present position of the slow sand filters, activated carbon is no longer necessary and will be eliminated eventually.

4.9 Post Chlorination

Chlorine dioxide produced from the reaction of hydrochloric acid and sodium chlorite is used.

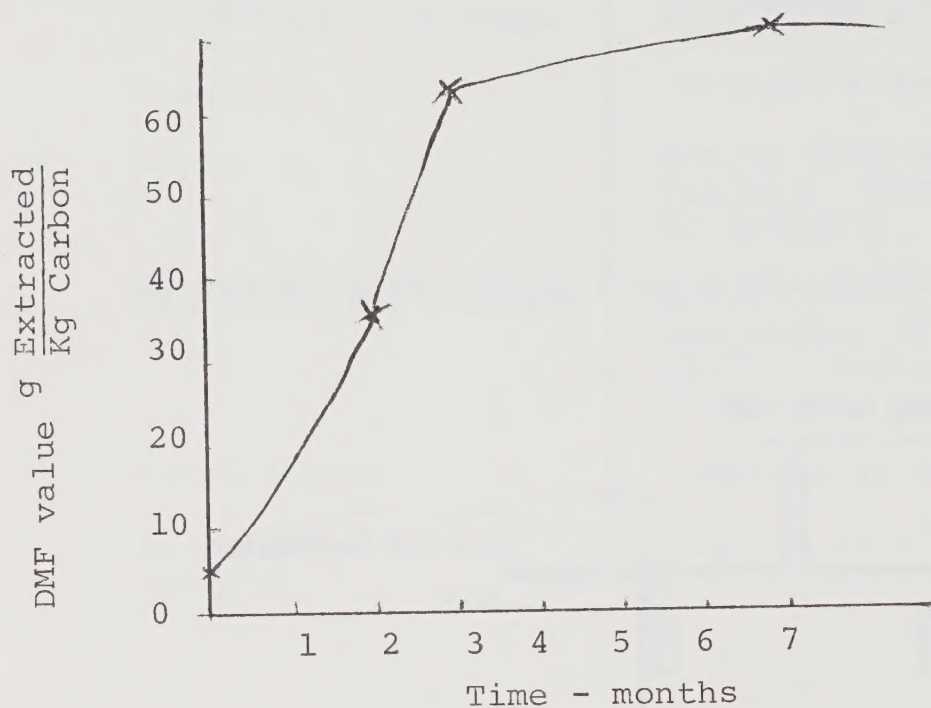
Dosage - controlled to 0.02-0.03 as residual chlorine by continuous monitors.

5. DISCUSSION OF ACTIVATED CARBON ADSORPTION

5.1 General Organic Removal

Organic Loading as Determined by DMF Extraction

varied between 4 g/kg (new carbon) to 68.5 g/kg (7 month used carbon).



5.2 Specific Organics

A large variety of organics have been identified in the intake, however, for the moment, details on their removal by carbon has not yet been obtained.

5.3 Biological Aspects

By backwashing twice a week, the reinfection of water by activated carbon has been maintained below 10-50 bacteria per cm³. Less frequent backwashing are believed to cause significant reinfection.

5. GENERAL COMMENTS

This plant contains many precautions such as:

- (i) A parallel gravity supplied water system, for the 800 fountains of Zurich, to insure the supply of drinking water in case of plant problems, and standby electrical power generation facilities.
- (ii) Routine granular carbon and ozone treatment as well as standby powdered carbon treatment to prevent the organic contamination of the drinking water.
- (iii) Fish living in tanks supplied by water from different parts of the plant, and
- (iv) Sterilization of air entering covered reservoirs.

The routine ozonation and granular carbon treatment are considered precautions as, in other parts of Europe and in North America, such treatment in view of the excellent raw water supply quality encountered at Lengg, would not be considered necessary. The Zurich water authority, however, considers that

'It is the duty of every water supplier to insure that the water quality derived from treated surface water is in no way inferior to an objectionable well water quality, particularly, with respect to organic substances' (Schalekamp, 1975).

The reference to well water is based on the work of Grob et al. (1974) who showed that the wide variety of organics found in Lake Zurich water are absent from well water.

In view of the above principle, the Lengg plant contains, in addition to the above organic removal stage, a final, slow filtration stage. Thus, the treated water is filtered three different times and, as a result, the removal in each stage is quite small (see Section 3). On the other hand, the treated water, is of such high quality, that a residual 0.02 to 0.03 mg/l post chlorination suffices to eliminate biological growth in the distribution system. The residual chlorination limit for Switzerland is 0.05 mg/l as Cl_2 .

The total capital and operating cost for this plant, assuming an annual capacity of $40 \times 10^6 \text{ m}^3$, was listed by Schalekamp (1975) as \$0.13/ m^3 . This cost is not exceptionally high by Canadian Standards and the reasons for this are:

- (i) excellent raw water quality (this would be often similar in Canada), and
- (ii) the direct filtration, practiced by the Lengg plant, eliminates the need for the costly slow mix and sedimentation tanks.

The cost of the activated carbon stage is one eighth of the total, or approximately \$0.016/ m^3 . Thus considering a Canadian family using $1.2 \cdot \text{m}^3/\text{day}$ the cost for this stage of treatment would amount to \$7.00/year.

The best measure of acceptability to Zurich waters of this kind of expenditure toward a safe and an aesthetic water supply is given by the results of a 1970 referendum, when Zurich voters voted 11 to 1 in favour of expanding the money required to improving their water supply system to its present high standard.

REFERENCE

Schalekamp, M. (1975). Translation of Reports on Special Problems of Water Technology, Vol. 9, Adsorption. Proceedings of a Conference held at the Engler Bunte Institute fur Wasser-Chemie, Karlsruhe, Fed. Rep. of Germany.

THE WATER TREATMENT PLANT OF THE SOCIÉTÉ LYONNAISE
DES EAUX ET DE L'ECLAIRAGE AT MORSANG-SUR-SEINE

1. WATER INTAKE

- Source - The Seine, about 20 km above Paris, just before its confluence with the Orge
- Raw Water Quality - Relatively poor (see section 3) and also, quite variable
- Flow - Flow in m³/d

	Current Avg.	Avg.	Design Peak
Wing 1	40,000	50,000	75,000
Wing 2	40,000	50,000	75,000

2. PLANT FLOWSHEET

The plant is constructed in a rather unique and aesthetic triangular style

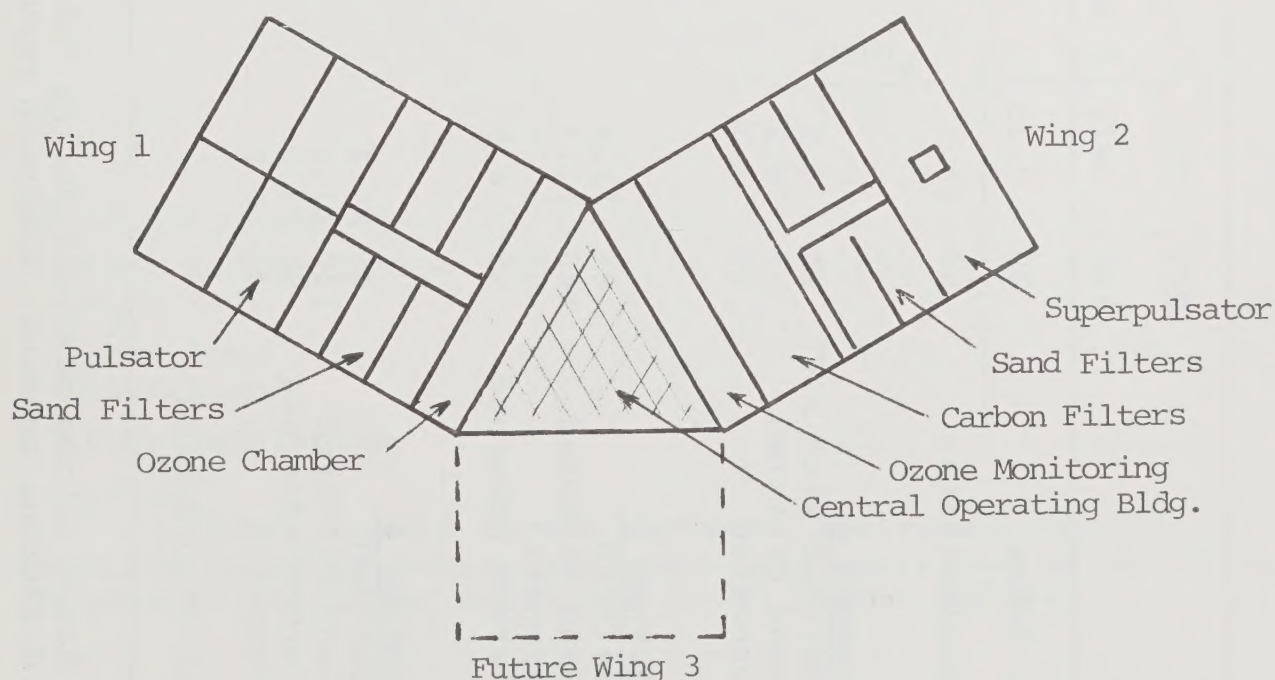


Figure 1: General Layout of the Morsang-sur-Seine Plant

SPECIFIC ORGANICS ANALYSIS

	Haloforms*					Pesticides**			
	CCl ₄ ng/l	CHCl ₃ µg/l	C ₂ H ₃ Cl ₃ ng/l	C ₂ Cl ₄ ng/l	CHBrCl ₂ ng/l	CH ₂ Br ₂ ng/l	Total ng/l	Organo- chloric ng/l	Organo- phosphoric ng/l
Raw Water	30	0.33	15	35	70	--		3.0	114
Prechlorinated	50	11.1	45	150	2.3	60		12.4	305
<u>Sequence 1</u>									
Settled with PAC	45	8.9	--	--	2.2	255		5.2	82
Sand Filtered	55	8.2	--	15	2.1	80		4.8	197
Ozonated	40	8.3	35	30	2.1	90		4.1	190
<u>Sequence 2</u>									
Settled	85	11.4	25	70	3.3	430		10.4	65
Sand Filtered	140	11.3	70	110	3.8	620		7.0	189
Ozonated	35	10.7	80	250	3.1	420		12.5	148
Carbon Adsorbed	55	6.9	--	45	3.1	540		4.1	220
<u>Sequence 3</u>									
Settled	85	11.4	25	70	3.3	430			
Sand Filtered	140	11.3	70	110	3.8	620			
Carbon Adsorbed	55	8.6	5	58	3.5	55			
Ozonated	40	6.9	40	35	2.6	325			
Post-Chlorinated								2.6	136

* Based on one analysis during February 1977 (other analyses were also available during different seasons, however, results were similar).

** Based on a single analysis during November 1975

The Central Operating Building contains Chemical Storage and Preparation Facilities, Ozone Preparation and Addition, and associated instrumentation. A small reception center is also located here. Another building, outside of the triangular complex, houses the laboratories, offices, the central control room, and the pumping station.

3. WATER QUALITY PARAMETERS

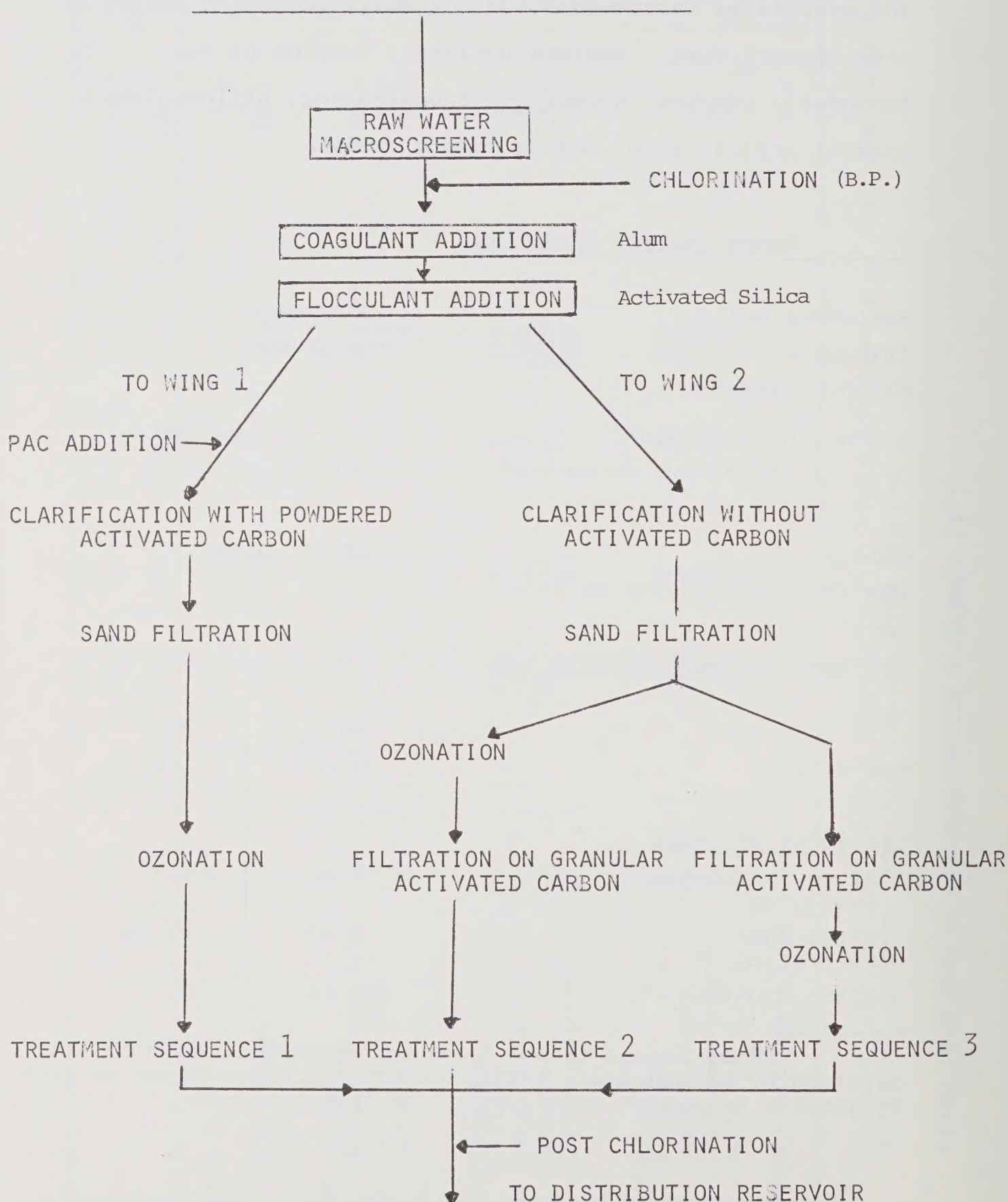
Suspended Solids	5-10 mg/l
Turbidity	5-80 JTU
Organic Matter	
KMnO_4^* no. (acidic)	2.5-4.5 mg/l as O_2
at 253.7 nm - 10 cm cell	1.6
Colour	20-25 (APHA)
TTN (Threshold Taste No.)	10-40

Average Treatment Results (over 17 months in 1976 and 1977)

	KMnO_4	TTN
Raw Water	3.50	22
<u>Treatment Sequence</u>		
After Sedimentation (with PAC)	1.60	4.5
After Sand Filtration	1.47	3-3.5
After Ozonation	1.22	3

* KMnO_4 number is the European equivalent to COD obtained by permanganate titration and expressed as mg of O_2 /l. In general acidified solutions yield higher values.

TREATMENT SCHEMATICS OF THE MORSANG WATER TREATMENT PLANT



Treatment Sequence 2

	KMnO ₄ no.	TTN
After Sedimentation	1.92	7
After Sand Filtration	1.68	5
After Ozonation	1.32	3
After Carbon Adsorption	0.98	1

Treatment Sequence 3

After Sedimentation	1.92	7
After Sand Filtration	1.68	5
After Carbon Adsorption	1.05	1-1.5
After Ozonation	1.05	1-1.5

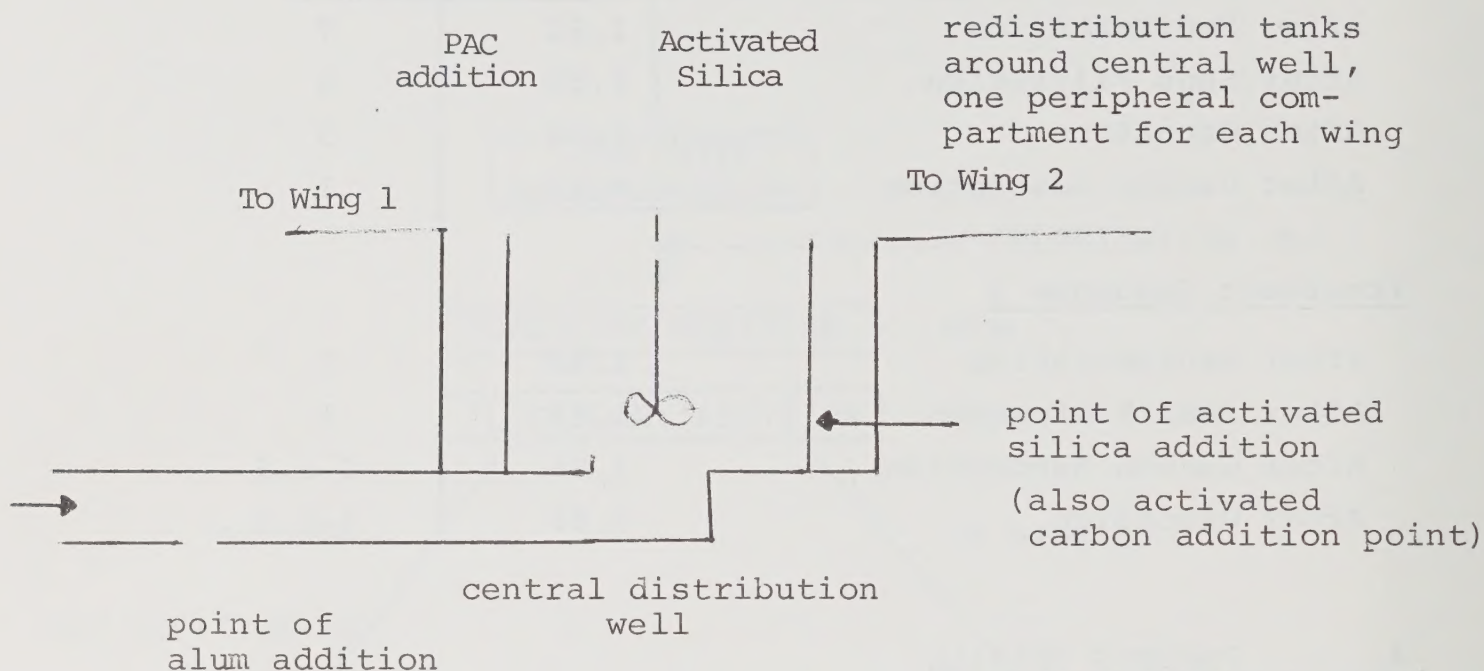
4. PROCESS DETAILS4.1 Pre-treatment

Straining: Bar screens are used on the water intake (a channel, along the shore line) which are rotated slowly.

Screening: Fine screen drums (macroscreens) rotated and water jet washed.

Prechlorination: At intake of pumps (water to pumping stations flows by gravity). Normal dosage of ~3.5 mg/l to breakpoint of ammonia elimination. Dosage is controlled by amperometric determination of breakpoint requirements.

4.2 Coagulation



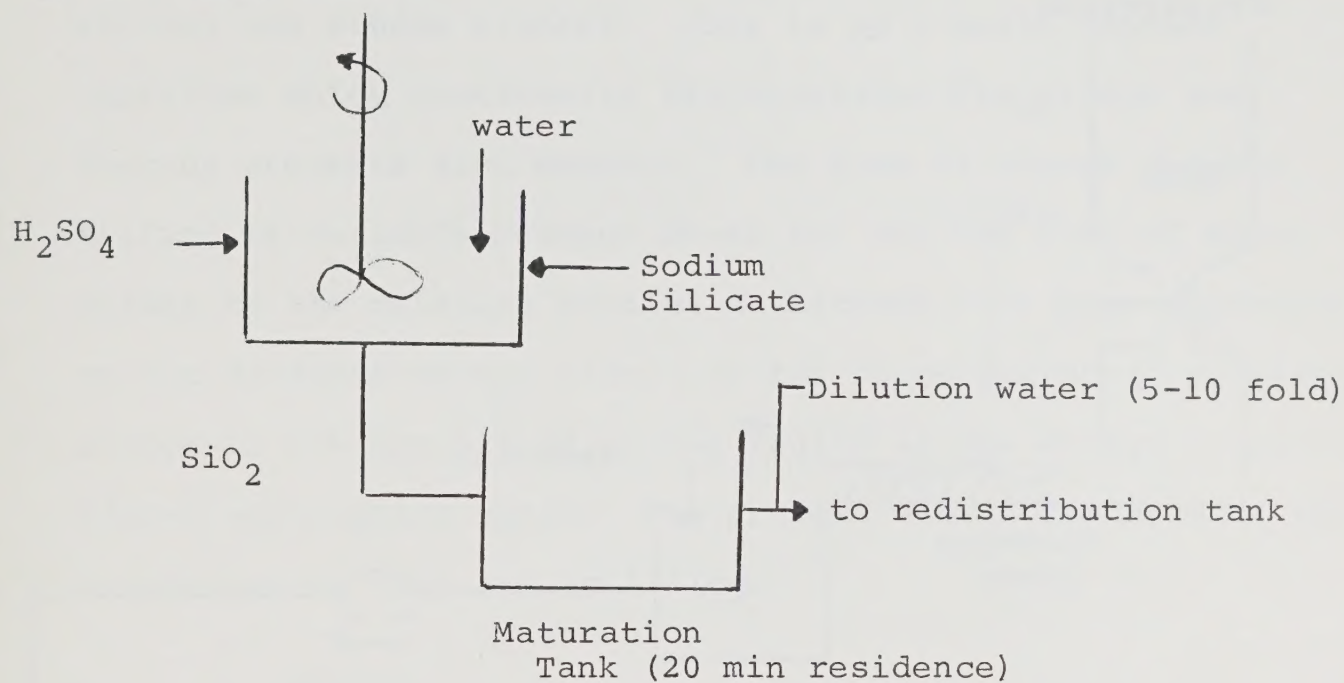
Coagulant - Aluminum sulphate

Dosage - 40-80 mg/l as $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$

Neither slow or rapid mixing is built separately for coagulation. The pipeline serves as a rapid mix chamber at water velocities of 1.2-1.5 m/sec. The central distribution well has too slow agitation and too short residence time (on the order of 30 sec) to serve as either a slow or rapid mix step in the conventional sense.

4.3 Flocculation

By Activated Silica



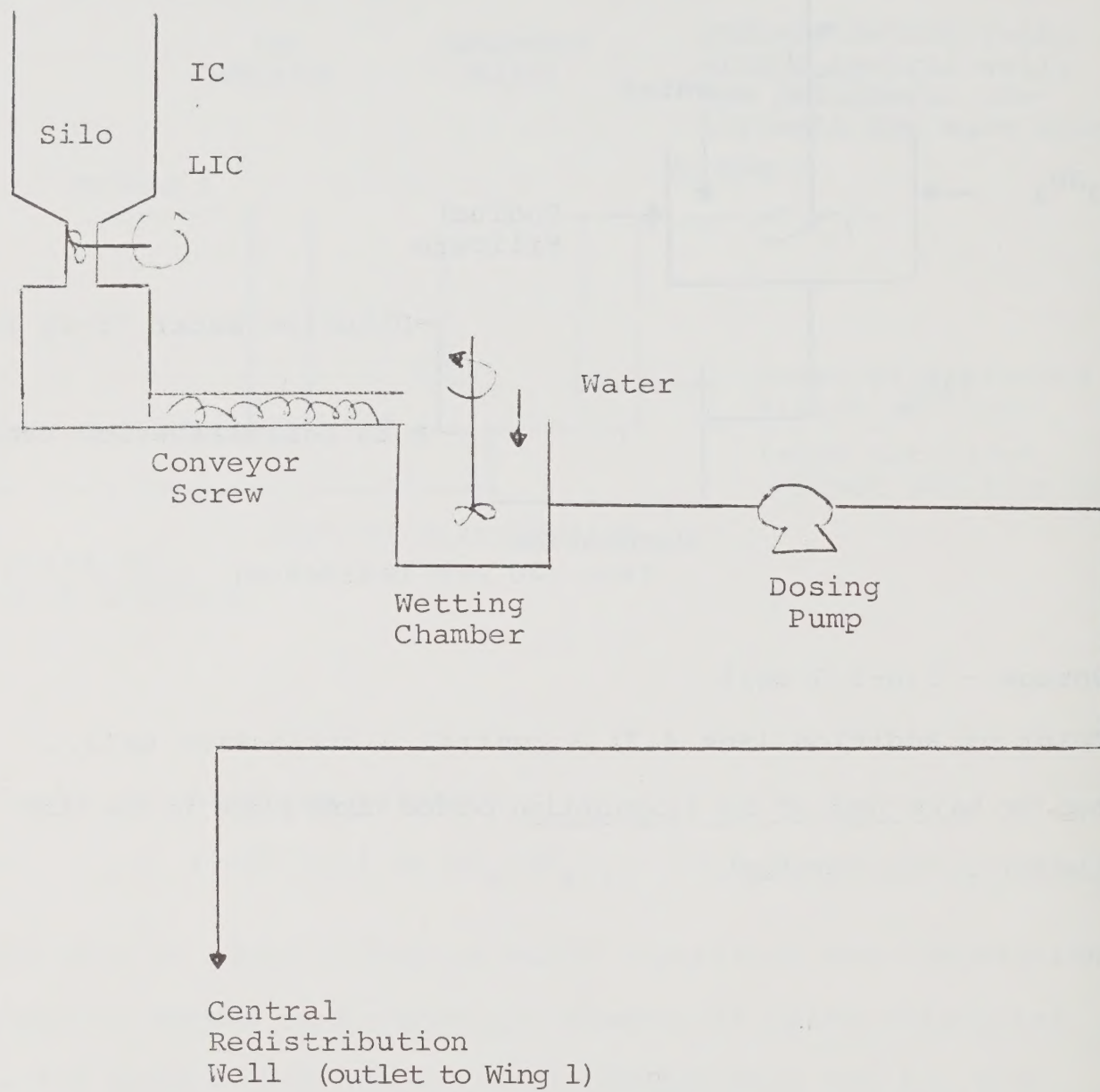
Dosage - 1.0-1.5 mg/l

Point of addition (see 4.2) - central distribution well.

but the major part of the flocculation period takes place in the floc blanket in the clarifier.

4.4 Powdered Carbon Adsorption

Preparation

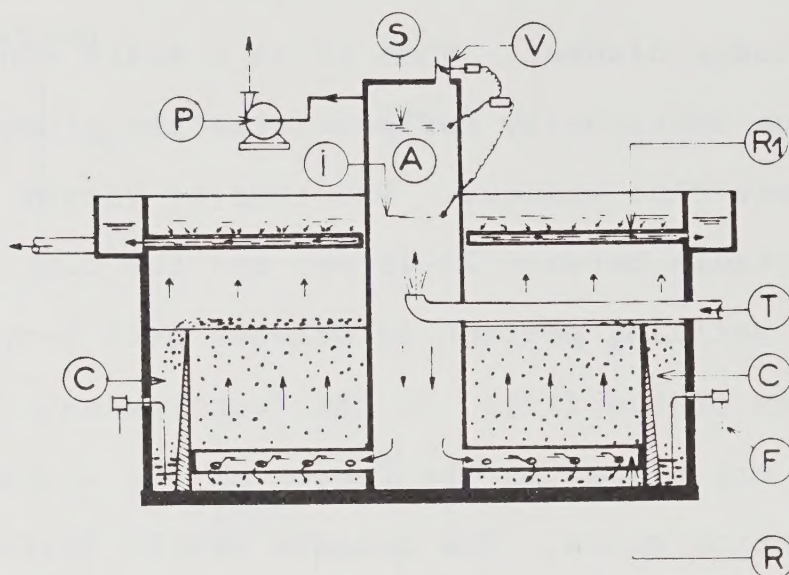


4.5 Sedimentation

Wing 1 uses a pulsator and Wing 2, a superpulsator. The pulsator, is a Degremont invention, and it consists of a central vacuum chamber which directs pulses of water upflow through the sludge blanket. Thus it is a solid contact clarifier which continually reflocculates the sludge and thereby prevents floc washout. The time of vacuum chamber filling is variable between 20-45 sec and the time of water pulses to the settling portion is between 5-10 sec, depending on the fineness of the floc. In the "superpulsator" parallel plates at 60% are placed in the region of the sludge to permit higher application rates. The process design features of the sedimentation tank are as follows:

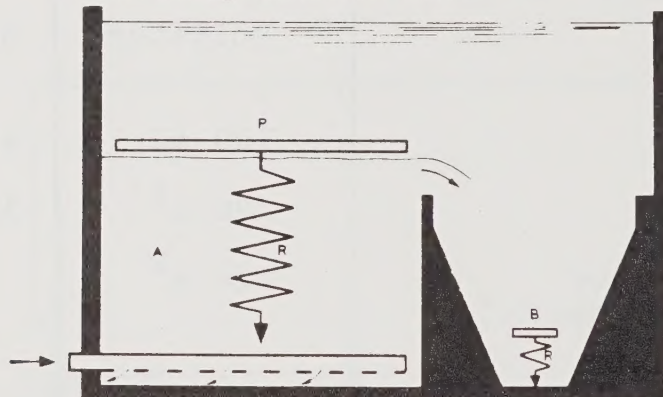
WING	1	2
Sedimentation Tank Type	Pulsator	Superpulsator
Total Surface	700 m ²	410 m ²
Settling Surface	590 m ²	314 m ²
Concentrator surface (incl.vacuum chamber)	110 m ²	96 m ²
Settling Velocity		
Based on Total Surface		
at 50,000 m ³ /d	3.2 m/h	5.4 m/h
80,000 m ³ /d	4.7 m/h	8.1 m/h
Based on Settling Surface		
at 50,000 m ³ /d	3.7 m/h	7.5 m/h
80,000 m ³ /d	5.6 m/h	11.2 m/h

The settling rates permissible in the pulsators is approximately 3-6 times above those typical of North American clarifiers.



- | | |
|--|------------------------|
| A. Bell. | P. Vacuum pump. |
| C. Sludge concentrators. | T. Raw water inlet. |
| R. Lower raw water distribution laterals. | V. Vent to atmosphere. |
| R1. Upper clarified-water collection channels. | |

How a sludge concentrator works



The spring R, pulling the piston P downwards, represents the force of cohesion of the sludge collected at A, this force being equal to the frictional force resulting from the ascending current of raw water passing through the sludge.

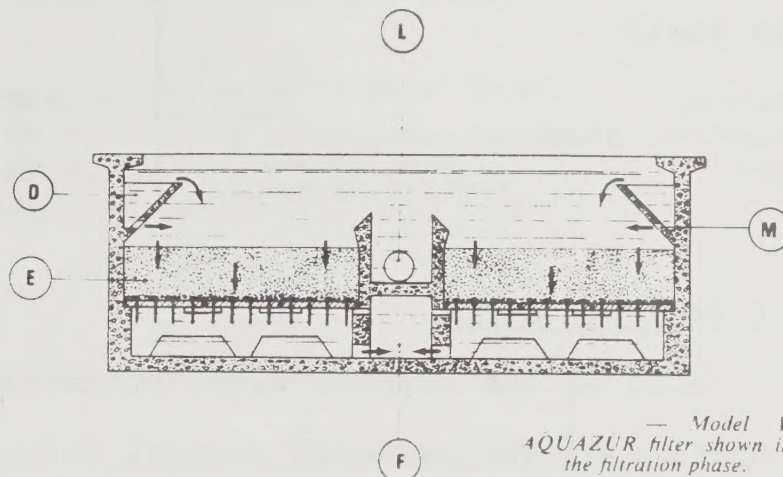
This force does not exist inside the sludge concentrator B where the spring R' represents the naturally-compacted sludge.

The sludge is then forced from the high-pressure zone A towards the low-pressure zone B.

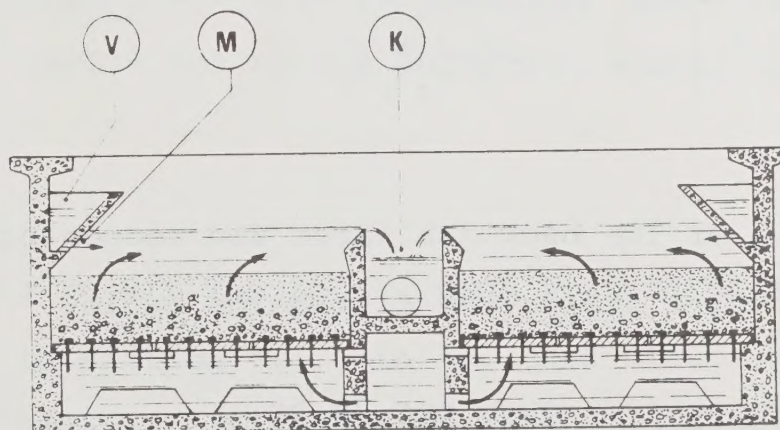
(a) The PULSATOR clarifier

4.6 Sand Filtration

The sand filters are Degremont Type V Filters. These filters that are furnished with cross flow feed inlet (see M in diagram) continue during backwash thereby ensuring efficient floc washout. This also signifies a high water level above filters to allow rapid filtration rates without gas pockets.



- E = Sand Bed
 D = Feed Materials - Shape V
 F = Filtered Water Channel
 K = Backwash Water Channel
 L = Wash Water Discharge Valve
 M = Orifices in V Laterals for backwash water cleansing



— Model V AQUAZUR filter (air/water scouring phase).

Process Parameters

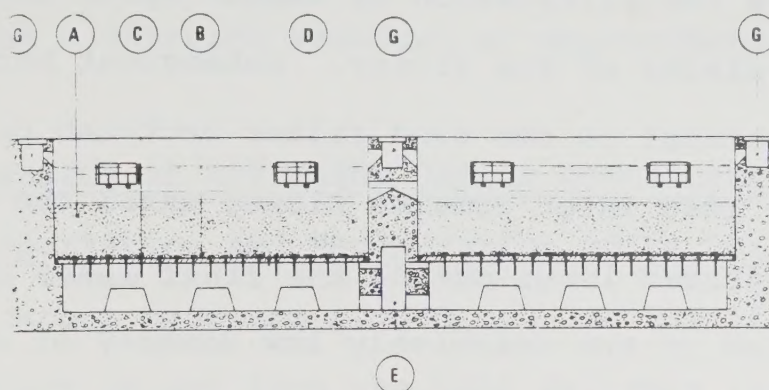
Wing	1	2
Number of filters	6	4
Surface per filter	60 m ²	63 m ²
Filtration Velocity		
at 50,000 m ³ /d	6 m/h	8.7 m/h
at 80,000 m ³ /d	9.2 m/h	13.1 m/h
Filter Media		
Material	sand	sand
Effective Size	0.95 mm	0.95 mm
Depth	0.80 m	1.0 m

Filter Backwash Steps

- (1) Closing of the treated water butterfly valve and the opening of the backwash channel valve.
- (2) Letting in water at 20 m/h together with air at 55 m/h, for 10 minutes then rinse with water alone at 20 m/h for an additional 5 minutes. During the entire backwash cycle settled water continues to arrive at the nominal application rate to insure crossflow across the filter.
- (3) Closing of the backwash water and reopening the treated water valve starts the filtration cycle.

Backwash Frequency: once per 20 hr.

4.7

Granular Activated Carbon Adsorption

— Model 'T' AQUAZUR dual filter with concrete floor and air water channel.

A. Sand.

B. Concrete floor.

C. Nozzles.

D. Water inlet clack-valves.

E. Air water distribution and filtered water outlet channel.

G. Sludge extraction channels.

Process Parameters

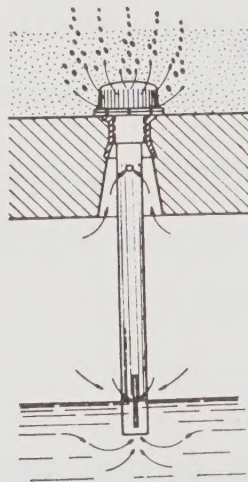
Wing	1	2
Treatment Sequence	2	3
No. of Adsorbers	2	2
Surface per adsorber	63 m ²	63 m ²
Filtration Velocity/Sequence		
at 35,000 m ³ /d	8.3 m/hr	8.3 m/hr
40,000 m ³ /d	13.2 m/hr	13.2 m/hr
Filter Media, Material	Filtrisorb 400	Filtrisorb 400
Effective Size	0.6 mm	0.6 mm
Depth	1.5 m	1.5 m

Backwash

Procedure is similar to the sand filters backwash cycle, outlined in section 4.6. In the case of the activated carbon filters, however, an effort is made to save the water already in the filter. Thus filtration is allowed to continue with the feed (clapet) and backwash drain valves closed until the water level is just a few centimeters above the carbon level. The filtered water valve is then closed and the backwash

drain is opened. Backwash water is then let in for 30 sec only to insure the elimination of vacuum spots developed during the draining of the filter. Subsequent backwash steps are identical to the sand filter backwash procedure, although, the feed inlet remains closed until the water level reaches the desired level during the final water backwash stage.

In view of the relatively low density of carbon, sudden bursts of air in the presence of water backwash can result in the loss of activated carbon to the backwash drain. Thus special air lines are incorporated in these filters to bleed air trapped below the distributor floor. Furthermore, special distributors have been developed by the Societe Lyonnaise, in conjunction with Degremont, such that the air below the distributor floor can only exit through these bleed lines.



Backwash water in

Backwash Frequency: once per 40 days

4.8 Residual Chlorination

Dissolved chlorine gas is applied to the final effluent to bring about a chlorine residual of approximately 0.2 mg/l.

5. DISCUSSION OF ACTIVATED CARBON ADSORPTION

5.1 Transportation and Regeneration of Carbon

The carbon beds are pumped out and refilled very simply by hydroejectors to and from the bulk delivery trucks used to transport carbon between the plant and the site of the regeneration furnace. Presently, regeneration takes place in the multiple hearth regeneration furnace of the carbon supplier, Chemviron, in Brussels. As intermediate storage tanks are not used, capital cost for equipment is essentially eliminated and operating cost, in terms of carbon loss, is minimized. Some plants use sand or gravel to protect the distributor nozzles and improve flow distribution during filtration.

In such plants, however, desanding prior to regeneration must be practised and this is not always easily accomplished. At Morsang, the adsorbers are filled with carbon only thereby the need for desanding, is eliminated. Based on results to date, plant personnel do not feel that either sand or gravel is necessary in the carbon filters.

5.2 Powdered versus Granular Carbon

Data from the two parallel wings permit a comparison of powdered versus granular carbon adsorption. Results, to date (Richard and Fissinger, 1977) indicate that while both powdered and granular carbon can usually produce an acceptable

effluent, this effluent is a much stronger function of influent concentrations in the case of the powdered carbon. Average dosages may be approximated at 20 and 4 g of carbon/m³ of treated water for the powdered and granular carbon respectively. A life of 2 years prior to regeneration is assumed for the granular carbon in this estimate.

5.3 Effect of Ozone on Carbon Adsorption

The two treatment sequences of Wing 2 were designed to evaluate the effect of ozonation on carbon. Richard and Fiessinger (1977) compared the relative efficacy of carbon before and after ozone and concluded that there appears to be only slightly better organics adsorption with pre-ozonation. The difference between pre-ozonation and post-ozonation is explained in a mechanistic sense in another article in preparation.

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- Richard, Y. and Fiessinger, F. (1976), La Technologie du Traitement des Eaux Potable par le Carbon Actif Granulé. Technique et Science Municipales, 70, No.7,8,9.

PLANT VISIT TO HOLTHAUSEN* POTABLE WATER TREATMENT PLANT
CITY OF DÜSSELDORF, GERMANY

1. WATER INTAKE

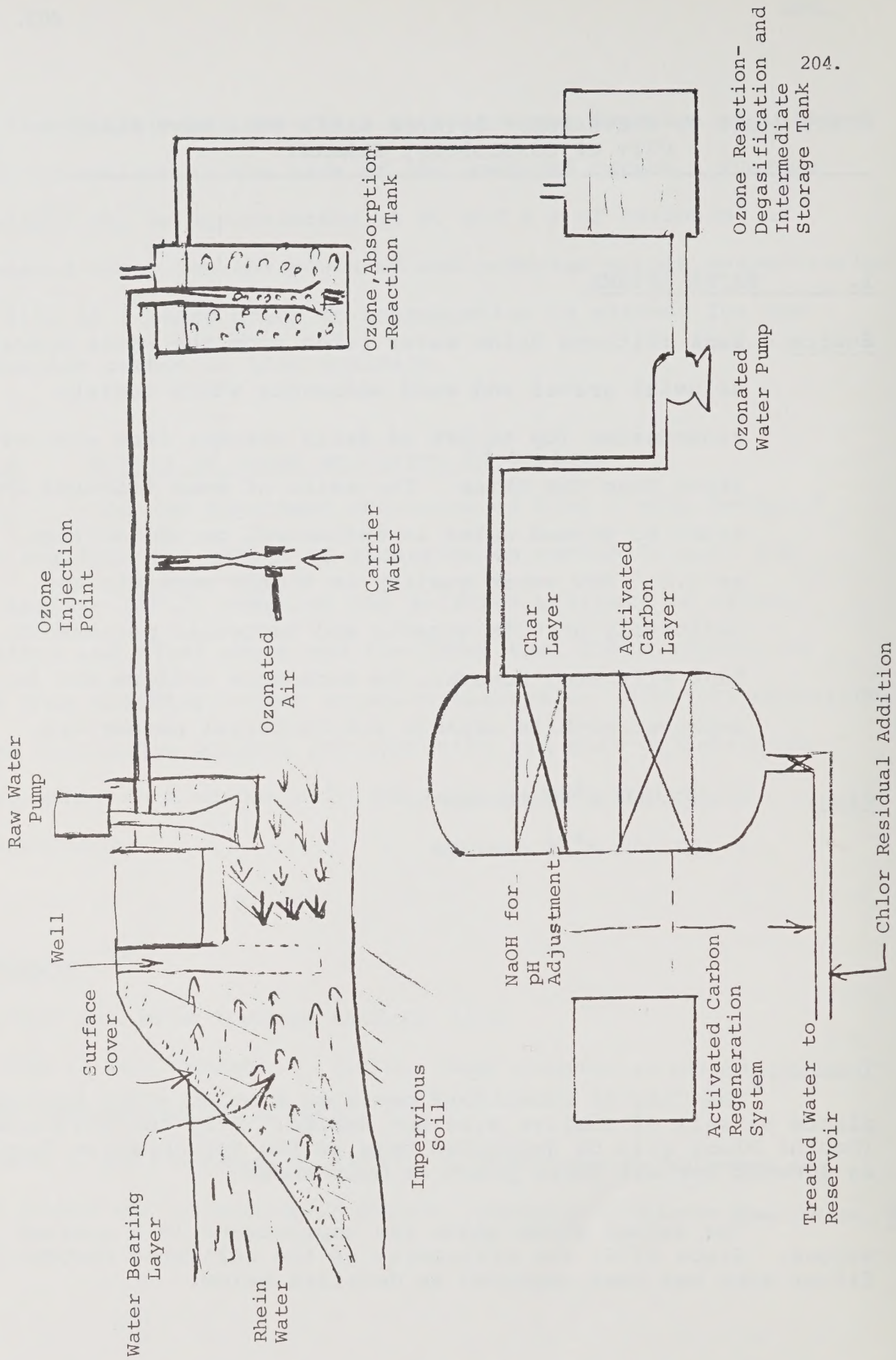
Source - Bank filtered Rhine water taken from the water bearing diluvial gravel and sand sediments which contain groundwater (up to 30% of daily intake) from sources other than the Rhine. The ratio of bank filtered Rhine water to ground water is estimated, on the average, as 3.2. Raw water quality is highly variable and relatively high in organic and bacterial parameters. Bank filtrate, however, is much more uniform and is improved both in organic and bacterial parameters.

Flow - 240,000 m³/d maximum
 ≈ 100,000 m³/d average

* The City of Düsseldorf operates 2 other water treatment plants as well of similar size and design. Only the Holthausen (South) Plant will be described here as the regeneration furnace is located for all three plant at Holthausen.

** The values shown above are approximate 1975 average values. Since 1975, the efficacy of the activated carbon filter step has been improved as detailed below.

2. PLANT FLOWSHEET



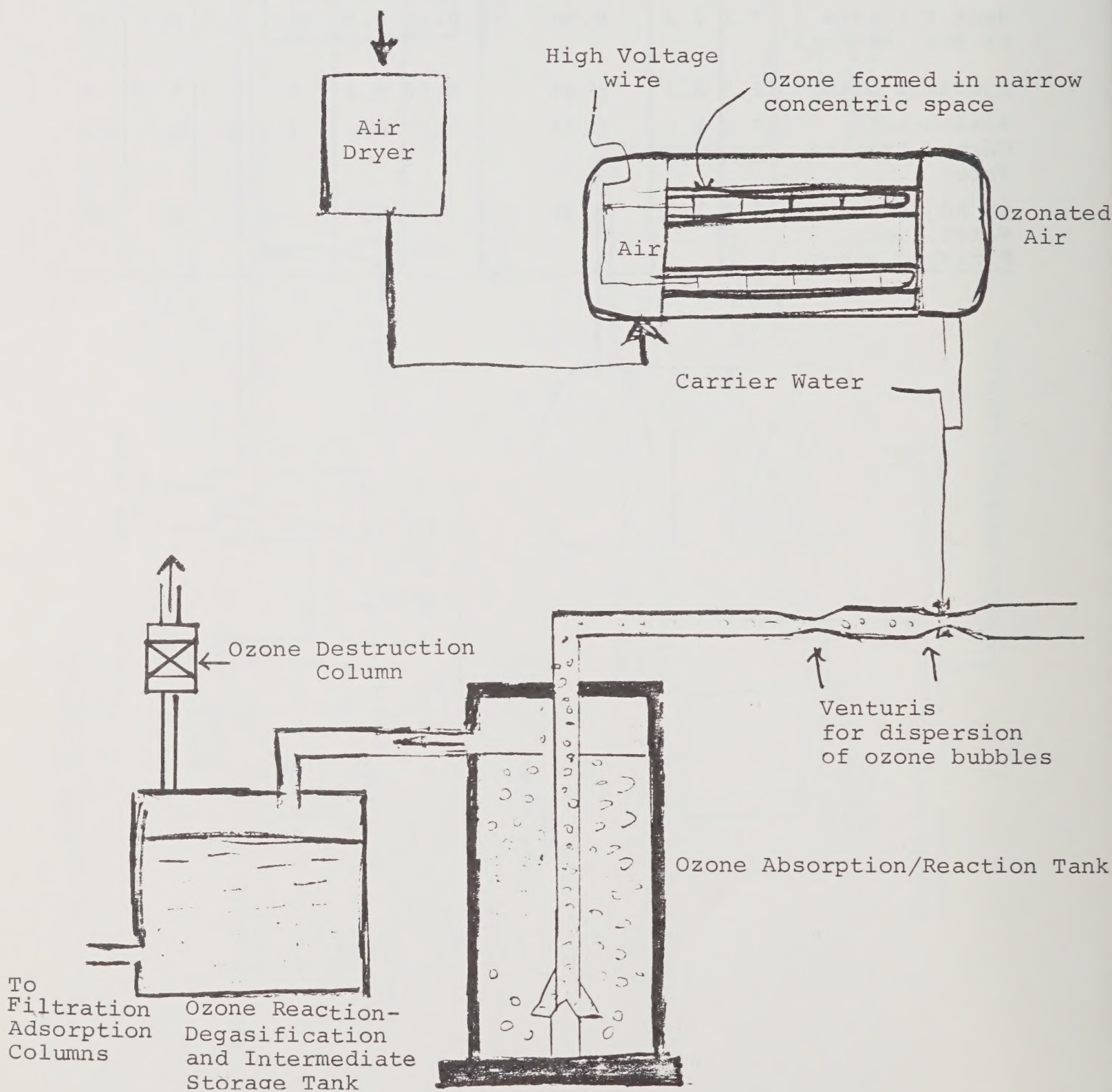
3. WATER QUALITY PARAMETERS**

	pH	DOC mg/l	UV DO of 10 cm at 250 mm	Fe mg/l	Mn mg/l	O ₂ mg/l	NH ₄ mg/l	NH ₂ mg/l	NO ₃ mg/l
Raw Water(Rhine)	7.4	6.1	1.10	1.5	--	5	2.3	--	14
Bank Filtrate or Well Water	7.1	2.3	0.50	0.06	0.4	≈1	≈1.2	0.1	14
Ozonated Water	7.1	2.2	0.25	0.06	0.4	8	≈1.2	0.05	9
Activated** Carbon Treated Water	7.1	1.7	0.15	0.03	ND	4	ND	ND	10
pH Adjusted Water,i.e., Finished Water	7.2	1.7	0.15	0.03	ND	4	ND	ND	10

4. PROCESS DETAILS

4.1 Ozonation

Flowsheet of Ozone Preparation and Addition



Dosage - 3 g ozone/m³ (increased from a former 1 g/m³)

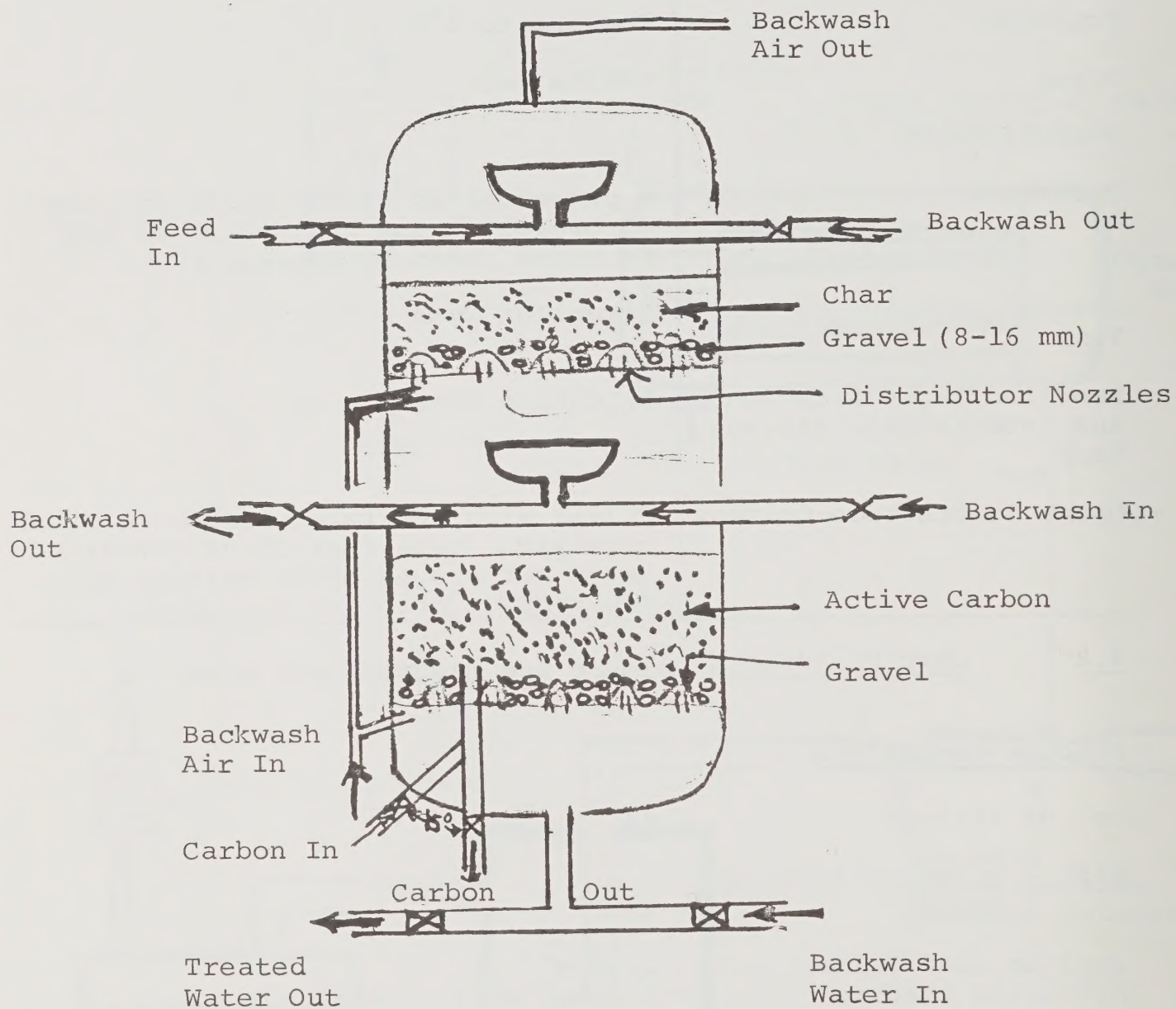
Equipment Details

<u>Equipment</u>	<u>Process Aspects</u>
Dust Filter	
Predryer	Cooling to 5°C
Dryer	Silica Gel
Dust Filters	
Ozonators	A potential of 16,000 volts are used to prepare a gas mixture of 35 g/m ³ of ozone (made by Herrmann)
Absorption/Reaction Tank	Detention Time = 5 min
Reaction/Degasification and Intermediate Storage Tank	Detention Time $\geq \frac{1}{2}$ hr
Ozone Destruction Columns	Filled with activated carbon or other catalyst. Less than 3% of generated ozone escapes to these columns for destruction prior to discharge.

4.2 Char Filtration (please see diagram next page)

Process Parameters

No. of filters	- 24
Size - diameter(internal)	- 5 m
- height	- 8 m
Surface area/filter	- 19.6 m ²
Hydraulic Loading	- 9 (avg) to 21 (max) m/h
Media	
type	- activated char
Depth	- 1.6 m
size distribution	- 0.9-2.5 (avg. size 1.7) mm
bulk density	- 580 kg/m ³

Char Filtration

Backwash

Procedure

- (i) Close water feed valve
- (ii) Drain filter to surface of Char
- (iii) Close valve
- (iv) Wash with air at 30 m/h for 2 min
- (v) Close air
- (vi) Wash with water alone at 15 m/h for 5 min
- (vii) Close water, start feed

Frequency - once every 24-40 hrs activated by pressure drop rising from 80 to 600 mbar

Backwash Treatment - backwash is pumped to batch decanters from where the supernatant is discharged to the sewer and the sludge is pumped to drying beds.

4.3 Activated Carbon Adsorption

Process Diagram - see bottom section of filter shown in Section 4.2.

Process Parameters

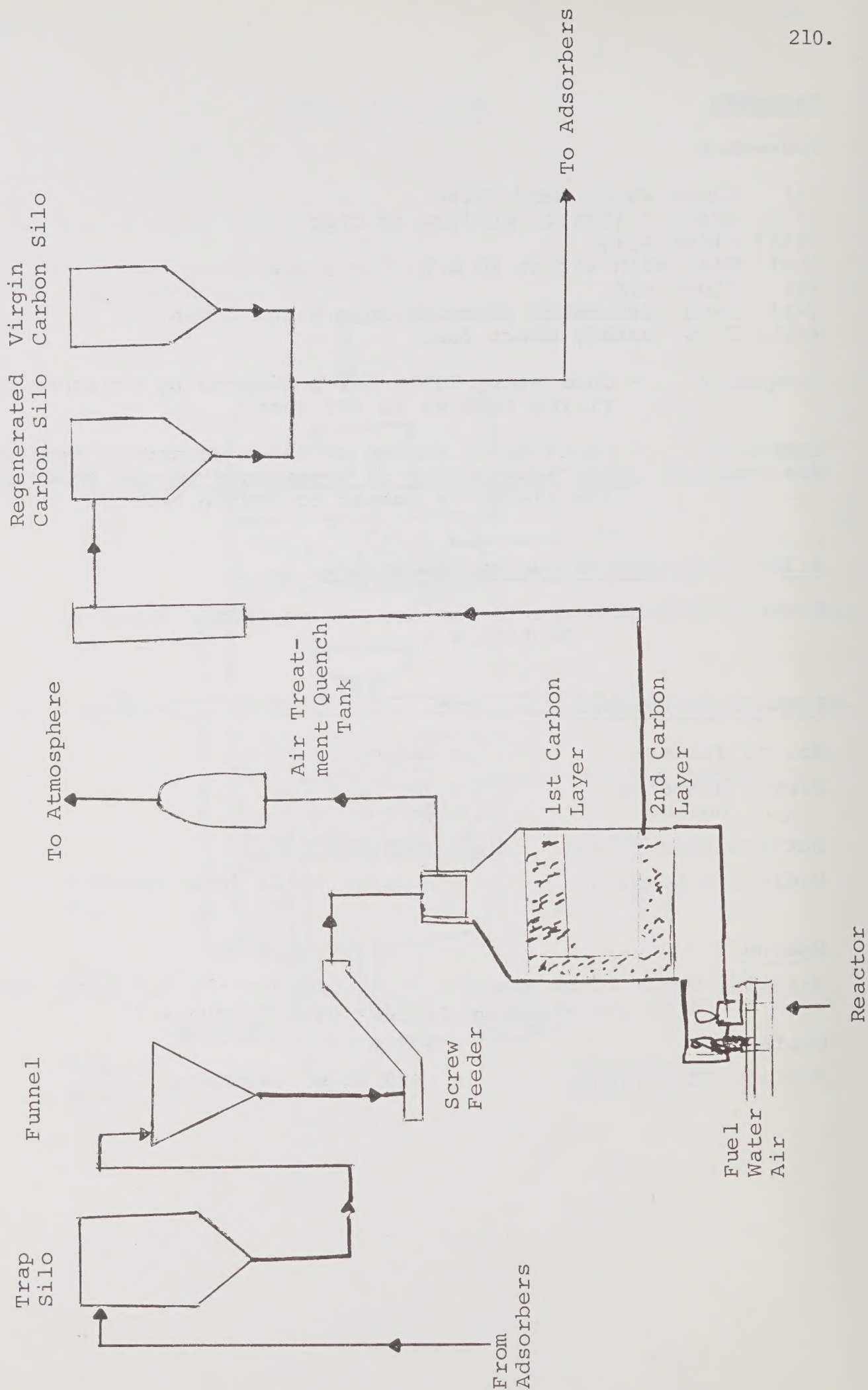
No. of filters	- 24
Size - diameter	- 5m
height	- 8m
Surface area/filter	- 19.6 m ²
Hydraulic Loading	- 9 (avg) to 21 (max) m/h

Medium

Material about 50:50 mixtured of Filtrasorb 300 and Lurgi LSS also individual with F300 or LSS separate)

Depth	- 2.5 m
Density of mixture	- $\approx 420 \text{ kg/m}^3$ (average)

4.4 ACTIVATED CARBON REGENERATION SYSTEM



Backwash

Procedure	- See section 4.2 for that of char filter. Before backwash begins with air, the water level is lowered to 10 cm above the carbon level, i.e., 40 cm below backwash outlet.
Frequency	- once per 4-6 weeks, backwash activated by pressure rising from 60 to 300 mb
Backwash Treatment	- see section 4.2.

Process Parameters

Equipment	Details
Spent Carbon	50 m ³ (=50 m ³ per filter)
Storage Trap Silo Silo Screw Feeder	45 m ³
Furnace	Capacity - 6 T/D Diameter - 0. m Feed rate (per regeneration hearth surface)= 500 kg/m ² -hr 1st layer operated between 200-300 °C with a 30 cm depth of carbon 2nd layer is operated between 700-800 °C and a 30 cm depth of carbon
Air Treatment	Multiclones and afterburner
Regenerated Carbon Storage	45 m ³
Make-up Carbon Storage	60 m ³

4.5 Final pH Adjustment

NaOH hydroxide is used to raise the pH to a point above the Langelier index (i.e., to eliminate aggressive carbon dioxide).

5. DISCUSSION OF ACTIVATED CARBON DATA

5.1 Carbon Loading

Criteria for exchange of carbon bed is based on UV absorbance, i.e., a carbon bed is sent for regeneration when less than 20% of the inlet optical density (UV at 254 nm) is removed. This will mean a carbon use of 30 g/m^3 of water filtered.

Assuming that UV optical density is proportional to TOC and assuming that an exponential relationship (as shown by Weissenhorn(1975)) is valid, this implies a $3.3 \text{ g TOC/g carbon}$ loading. The standard of $30 \text{ g of carbon/m}^3$ of water is planned for the near future as the regeneration furnace operation is normalized. Presently 15 g/m^3 is used and previously only 3 g/m^3 were used.

5.2 Specific Organic Adsorption

A recent article Poggenburg et al. (1976) discusses some pilot results at the Flehe treatment plant of the City of Düsseldorf just adjacent to its Holhausen plant. A gas chromatographic analysis of the exhausted carbon dioxane extract led to the following results:

	Range for 3 Different Carbons mg/m ³ *
1,2 - Dichlorethane	0.05 - 0.23
1,2 - Dichloropropane	0.21 - 0.52
Trichloroethylene	0.36 - 3.06
Tetrachloroethylene	0.46 - 0.82
Bis-(2-chlorisopropyl) -ether	3.88 - 8.81
0-Dichlorobenzol	0.13 - 0.27
Hexachlorobutadiene	0.74 - 1.79
Hexachlorocyclohexane	0.11 - 0.18
Tris-(2-chloroethyl) -phosphate	0.83 - 1.21
Total weight of defined compounds	7.7 - 17.8
Total weight of defined compounds expressed as mg of chlorine/m ³	3.9 - 9.6
Total weight of adsorbed organic chlorine	23 - 40
Total weight of extract- able organics (Dioxane and DMF)	1150 - 1450

* Based on m³ of water passed through the carbon filter.

5.3 Transportation of Carbon

Carbon is flushed out of each filter in 3 hrs (40 m³ of carbon). Synthetic materials are used for the pipeline and "quick disconnect" connections are manually joined to each filter prior to carbon exchange. Carbon is slurried with an approximately 3:1 volumetric ratio of water to carbon. The loss in transportation by trucks to and from an off-site regeneration furnace has been previously established as 15%. With on-site regeneration, this loss is expected to decrease to less than 10%. The carbon transport system is fully automated

computer controlled. At the present time, some initial problems (particularly with level controls) need to be smoothened out still.

APPENDIX C
ANALYTICAL TECHNIQUES

APPENDIX C
ANALYTICAL METHODS

TOC

Economic considerations forced the use of a TOC analytical system utilizing the adsorbance of UV light at 253.7 nm wavelength, by the organics present in water. Dobbs et al. (1972) showed that such a system is reliable and accurate for the analysis of potable waters. The data presented by Dobbs shows that increased sensitivity can be obtained by the use of a sample cell longer than the 5 cm sample cell used by Dobbs. Bausch and Lomb's Spectronic 21-UVD Spectrophotometer, the instrument used in this study, has the versatility to use sample cells up to 10 cm.

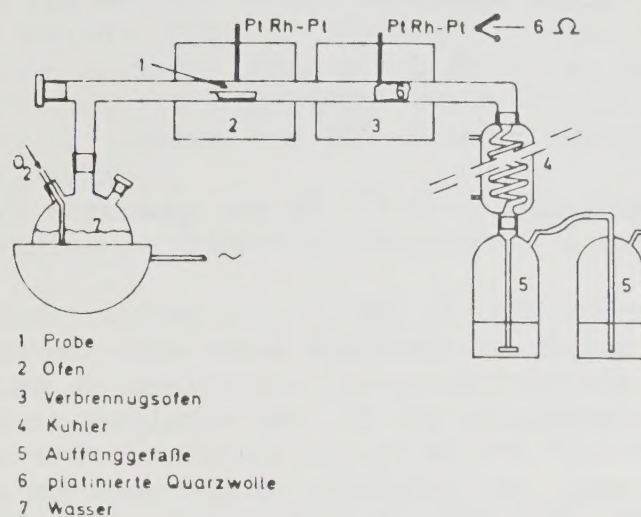
Initial instrument start-up data indicated that a reliable zero base line was impossible to obtain due to the lack of organics free distilled water. Thus the absorbance of the empty cell has been set at 0.100 for all TOC determinations.

The instrument was calibrated against the TOC analyzer of Goulden (1972) at CCIW. The calibration curve is shown in Figure III-1.1. TOC
10 cm
versus A correlation appears to be excellent.
254 nm

TOCl

The lumped parameter, total organic chlorine (TOCl) measurement was based on the method of Kuhn and Sontheimer (1973).

FIGURE C-1: Pyrohydrolysis Apparatus (from Kuhn & Sontheimer, 1973)



Versuchsanordnung zur Pyrohydrolyse.

- 1, sample boat
- 2,3, furnace
- 4, condenser
- 5, collection bottles
- 6, platinized quartz wool
- 7, water

The organics in the water are adsorbed onto activated carbon in columns. A sample of the carbon is air dried, and carbon water content determined by drying the air dried sample at 103°C . Of the air dried carbon sample, 5 gm is placed in 100 ml 0.1 N NaNO_3 solution and shaken overnight to desorb the inorganic chloride off the carbon. In parallel, 1 gm of airdried carbon is pyrolyzed at 900°C in the apparatus shown in Figure C-1.

The organics on the carbon are oxidized along with the carbon, and the molecular fragments containing the Cl^- are catalyzed to release the Cl^- on the platinized quartz wool and hydrolyze in the presence of H_2O to form HCl . The high temperature reaction products are condensed and collected in 0.01 HNO_3 solution containing 0.5 ml H_2O_2 . The chloride concentration in all solutions were determined by chloride specific electrodes. The oxygen to the apparatus is fed at the rate of 200 ml/min and the steam of 100 ml/hr.

The chloride level obtained from the desorption in NaNO_3 is subtracted from the chloride level obtained by pyrohydrolysis resulting in an organic chloride level.

The strict observance of this method leads to drastically high organic chlorine levels. The high levels cannot be accounted for by TOC balance from Table III-1.2. The possible presence of chloramines also could not explain the high TOCl levels as the chloramine level in the authors' laboratory tap water was about .1 ppm, in the raw water none was detectable and by the time the carbon sample was analyzed, the chloramines have reacted and the reaction products, N_2 and HCl , have probably escaped from the carbon (see Atkins, 1973).

Interferences with the Cl^- analysis by $\text{S}^{=}$ have been documented and its elimination before Cl^- analysis is advised (Standard Methods, 1975). The $\text{S}^{=}$ could emanate from the coal based carbon. The HNO_3 from the collection solution was eliminated while the 0.5 ml H_2O_2 was retained and 10 mg/l CaSO_4 added.

The carbon is loaded in batch of 10 l water containing 15 gm of granular carbon. A quantity (1 gm) of this carbon was shaken in 0.1 N NaNO_3 overnight to desorb the inorganic chloride. The residual solution was decanted and the carbon air dried and directly pyrohydrolyzed. The results are shown in Table III-1.3. The TOCl levels appear much more reasonable than those obtained previously. Nonetheless, there are still questions that were not answered, such as, have all the interferences been eliminated, the pH of the collection solution indicates that they may not have been, or have all the inorganic chloride have been eliminated. In a discussion, Dressman (1977) of the EPA has indicated similar problems with the method.

In view of the above problem, a separate and thorough investigation of the method should be undertaken before the validity of these results can be quantitatively accepted.

PAH

The authors PAH analysis was based on Borneff's (1969) TLC method, with slight modifications, as follows:

(i) Extraction. Sample, size of 10 l if TOC is high and 25 l otherwise was extracted with 60 ml/l cyclohexane by stirring at high rate for a half hour. The solvent and aqueous layers were allowed to separate

and the solvent layer syphoned off. The cyclohexane layer was dried by passing it through a column of dehydrated Na_2SO_4 .

(ii) Sample Concentration. The dry extract was concentrated in a vacuum rotary evaporator at 38°C to about 100 ml and transferred to smaller flask, and first flask rinsed to transfer all of the extract, and further concentrated to 10-20 μl . This volume was transferred to the TLC plates.

The flask was rinsed with aliquots of 5-10 μl cyclohexane, and transferred to the TLC plate until the contents of the flask and the syringe has shown no fluorescence at 366 nm.

(iii) TLC Plate Development. Plate: Al_2O_3 , 0.25 mm x 20 cm x 20 cm. Both the unknown sample and calibration standards were spotted on the plate. The plate was developed with hexane-benzene (5/2) mixture. The solvent front was allowed to advance 15 cm and the plate was viewed under 366 nm UV light. The fluorescent areas were removed from the plate and extracted with cyclohexane. The extract was spotted and developed on the plate with hexane-benzene (5/1) mixture. Then the plates were viewed under 366 nm and R_F values noted.

(iv) Compound Identification. Unknown compounds were identified by comparing their spot positions and colour with that of the calibration standards.

(v) Quantification of Identified PAH. The plot of the log of the amount of PAH standard spotted on the plate versus the square root of the corresponding spot area resulted in a linear function.

The spot area of the identified PAH thus provided its concentration in the original water sample, when compared against the corresponding calibration plot.

The results are shown in Table III-1.4. The data shows inconsistencies as the PAH concentrations increase after water treatment, including activated carbon, while the opposite is expected. Interferences from other organics, humic substances, in the raw water seems plausible. Saxena (1977) has substituted the adsorption of PAH onto polyurethane foam and extraction off the foam for the direct solvent extraction from the water samples. The PAH selectively adsorb onto the polyurethane foam while humic substances do not. The interferences were to a great extent eliminated.

This improved method was revealed too late for the authors to utilize for this study. Therefore, as fluoranthene was the most discernable PAH, total spot areas were expressed in terms of fluoranthene.

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A STUDY OF THE REMOVAL OF SYNTHETIC ORGANICS

**RESOURCE CENTRE
INST. FOR ENVIRON'L. STUDIES
UNIVERSITY OF TORONTO**



